A COMPARATIVE STUDY OF THE EFFECTS OF APPLYING ACRYLICS AND SILANES IN SEQUENCE AND IN MIXTURE, WITH A CASE STUDY OF THE COLUMN IN THE CONVENTO OF MISSION SAN JOSÉ Y SAN MIGUEL DE AGUAYO, TEXAS

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Abstract

A limestone column at Mission San José y San Miguel de Aguayo, San Antonio, Texas, exhibited extensive friability, microcracking, and flaking, and required conservation. Mixtures of acrylic resins and alkyl alkoxysilanes are frequently used for the consolidation and protection of friable, flaking stone, and with consistently good results. However, the deterioration of the column was localized and it was not advisable to introduce the adverse effects of the acrylic in the mixture to relatively sound areas. Also, the adhesion of subsequent infills would be adversely affected by the water-repellency of the alkyl alkoxysilane in the mixture. Sequential applications of the acrylic and the alkyl alkoxysilane would be more practical, flexible, and potentially more effeective. But published work was scant on the use of acrylics and alkyl alkoxysilanes in sequential order; the interaction of these two substances and their ultimate effectiveness when used in this manner was little studied. An experimental program was designed to determine if any differences in certain physical and mechanical properties of treated facsimiles were caused by the application of an acrylic and an alkyl alkoxysilane in sequence rather than in mixture. Preliminary test results indicate that, although mixtures may be somewhat more effective, the method of application does not greatly affect the new properties of the treated facsimiles. Based upon the experimental results and upon the deterioration patterns and treatment requirements of the column, preliminary consolidation with a deeply-penetrating ethyl silicate followed by a sequential application of an acrylic resin and an alkyl alkoxysilane was used for the conservation treatment of the limestone.

Preface

The following study was initiated after a decision was made to conserve a limestone column in the convento of Mission San José y San Miguel de Aguayo in San Antonio Missions National Historical Park, Texas. The material displayed the loss of intergranular cohesion, microcracking, and flaking characteristic of salt-contaminated stone. However, levels of deterioration within the column were variable and localized in association with gypsum bedding and patching mortars; relatively sound areas did not require the same types of treatment as massively deteriorated areas.

In recent years, mixtures of acrylics and alkyl alkoxysilanes have frequently been employed for the conservation of friable and flaking stone. Applications of mixtures combine the consolidative and water-repellent properties of alkyl alkoxysilanes and the consolidative and adhesive properties of acrylics in a single treatment. Although not perfect and variable in effectiveness from stone to stone, mixtures often satisfy more of the commonly-recognized criteria for stone consolidants than any other single treatment. Thus an acrylic and an alkyl alkoxysilane were selected as two of the basic conservation materials for the column stone.

But the deterioration of the convento column was localized. While the uniform application of a mixture of acrylic and silane would effectively consolidate the deteriorated areas, the acrylic would also unnecessarily (and negatively) alter the properties of relatively sound areas. Massive losses of stone in certain areas also dictated the use of infills to reestablish the structural and visual integrity of the column; the water-repellent properties of the silane in the mixture would inhibit the adhesion of these fills to

previously-treated stone. Because of the particular circumstances, it was felt that sequential applications of acrylics and alkyl alkoxysilanes would allow for greater flexibility in treating different levels of deterioration and would allow for the effective application of infills. However, few experimental programs or treatments have been published in which sequential treatments of acrylics and silanes were tested or used; the relative effectiveness of this method of application was not well-studied.

An experimental program was designed to compare the differences in the properties of sequences and mixtures as a result of their chemical interaction, and also to compare the effects of the method of application on the physical and mechanical properties of the treated object. The ultimate objective of the experimental program was to determine if sequential applications of acrylics and alkyl alkoxysilanes were as effective as mixtures for the conservation of stone. Samples of weathered stone could not be taken from the column, and artificial facsimiles, rather than unweathered stone samples, were used in the experimental program because they could provide more measurable and statistically comparable results. Thus, while the quantitative results of the experimental program were not directly applicable to the column stone, qualitative comparisons between the two treatment methods were relevant. The final selection of a treatment for the convento column was based upon the results of the experimental program as well as on the particular deterioration phenomona and treatment requirements of the limestone.

Chapter 1. Alkoxysilanes, Acrylics, and their Mixtures: History, Characterization, and Use for the Conservation of Stone

1.1 Overview

The conservation of stone is an old practice - the first known written record of materials and methods for stone preservation is given by Vitruvius in the first century B.C. But there was little deviation from traditional practices until the early nineteenth century, when the environmental consequences of the industrial revolution were observed on stone edifices in the urban industrial centers of Europe. To combat the rapid decay of the stone and to preserve buildings and monuments alike, chemists began to experiment with a variety of inorganic and organic materials. A few of their proposed treatments appeared to work for a time but most did not, resulting in a sense of frustration in the face of stone decay by the middle of this century. With renewed concern and interest in the 1960s and 1970s, old conservation materials were reexamined and new products and methods were developed, resulting in the availability of a wide array of conservation materials. Many of these were not rigorously tested prior to use nor proven to age well, and the following decades saw the field application of this wide array of materials with an even wider array of results.

Through the long-term evaluation of the results of those early field applications and also through continued trial and error, alkoxysilanes and acrylics have emerged as the preferred conservation materials for stone. Although far from perfect, they have been

submitted to extensive testing and characterization and have proven reliable and effective in many practical situations. The alkoxysilanes, depending upon their chemical composition, can consolidate and/or impart water repellency. The acrylics possess both consolidative and water-repellent properties, but are also valued for their ability to readhere flakes and larger grains of stone.

In 1976, Nonfarmale reported the successful treatment of a sandstone using a mixture of an alkyl alkoxysilane and an acrylic. Since then, conservators have frequently employed such mixtures, both custom and proprietary, for the treatment of friable and flaking stone. Only recently, however, were the chemical interactions of these components investigated and the effects of these interactions on their physical and mechanical properties understood. The mixture of alkyl alkoxysilanes and acrylics does alter certain physical and mechanical properties of the individual substances, and thus alters their capacity to preserve the stone to which they are applied.

The question then arose as to how alkoxysilanes and acrylics would affect each other if applied sequentially - as two phases of a single treatment - rather than as a mixture, and if the effectiveness of the treatment would be the same. No comparative studies were found nor were any sequential treatments documented in the literature. Thus an experimental program was designed to open an investigation into the different interactions, if any, between an alkyl alkoxysilane and an acrylic when applied as a sequence and as a mixture, and the relative effects of these two methods of application on the physical and mechanical properties of a treated stone.

1.2 Brief history of materials used for the conservation of stone

Early methods of stone conservation were based upon the application of a protective coat which was frequently water-repellent. Perhaps the earliest method of stone preservation, whether intentional or not, was the plastering and/or painting of stone architectural elements and the painting of stone sculpture. No written records have yet been uncovered which indicate the intentional use of paint or any other material as a protective coat for stone prior to the classical Roman period.

In the course of investigating the 15th century sculptures by Jacopo della Quercia in the portal of San Petronio, Bologna, prior to restoration, Rossi-Manaresi (1972) discovered the presence of an original protective film composed of wax (probably beeswax), resin (colophony or sandarac), and possibly rue oil. This discovery led to a search of historic literature for references to "antique" protective treatments for stone sculptures. The first direct reference to stone preservation was given in the first century B.C. in The Ten Books on Architecture, in which Vitruvius stated that naked marble statues were protected with wax melted and mixed with a little oil. Practical handbooks and books of recipes written in Italy between the 10th and 17th centuries were also studied, as were more formal treatises on sculptural technique by prominent authors such as Vasari and Cellini. The survey uncovered only two possible references to protective coatings for stone: the first, called *cera colla*, was possibly a mixture of wax and resin, and the second was a varnish containing sandarac, nut oil, incense, and potash alum (Rossi-Manaresi, 1972).

Most discoveries of the use of preservatives have arisen from the investigation not of the historic literature but of the historic buildings. For instance, through site investigations it is known that beeswax was used to protect stone sculptures on mediaeval cathedrals

(Weber and Zinsmeister, 1991). Few, if any, surveys of pre-19th century period literature on stone preservation have been published; thus little else is known about the early use of materials for the preservation of stone, or indeed whether the conscious intent existed. As Horie (1990) notes, "The concept of conservation, that the original object is intrinsically interesting and worth preserving, has been widespread only in the past few hundred years."

Increasing concern for the preservation of stone sculpture and monuments arose in the early 19th century, and with it began the development of methods and materials for stone preservation.

> It was in the urban areas of the arising European industrial countries...that the phenomenon of this "pathological" stone deterioration was first observed. Soon, increased atmospheric pollution was suspected to be the main reason for the new "stone disease." Limestones and lime-bound sandstones appeared to be affected preferentially by the typical symptoms, such as black crust formations and the loss of internal strength. In many cases the traditional stone-mason's practice of replacing damaged stones with new ones was no longer compatible with the velocity of decay and the immediate and dire need to repair vast surfaces. The young chemical industry did not delay in developing procedures intended to stabilize the weathered materials (Schmid, n.d.).

Over the course of the past two centuries, inorganic, natural organic, and synthetic organic materials have been developed, refined, and often discarded for use as consolidants and protective coatings for natural stone. The following is a general list of those materials, categorized by the nature of the raw materials from which the end product is then derived:

Inorganic:	alkaline silicates (sodium silicate or "waterglass," potassium silicate, zinc and magnesium fluorosilicates)

hydroxides (barium, strontium, calcium)
acids (hydrofluoric, phosphoric)
stearates (zinc and aluminum)
salts (calcium chloride, aluminum sulphate, calcium sulfate)

Natural organic: glues and gelatins
waxes and paraffins
resins
oils (linseed and poppyseed)

Synthetic organic: acrylics
epoxies
alkoxysilanes (ethyl silicate, alkyl alkoxysilanes, siloxanes, silicones)
vinyl polymers [poly(vinyl acetate), poly(vinyl chloride), etc.]

With the exception of epoxies, all of the above conservation treatments were developed and applied in some form prior to the 1950s (Horie, 1990). A few of these treatments appeared to work for a time but most did not, resulting in a sense of frustration and helplessness on behalf of the caretakers of historic stone monuments and buildings by the middle of this century (Schmid, n.d.). With the renewed concern and interest in stone preservation which arose in the 1960s and 1970s, many old conservation materials were reexamined and new products were developed as well, resulting in the availability of a wide array of conservation materials (Zinsmeister et al., 1988). Many of these were not

tested and characterized extensively in laboratory situations nor proven to age well. The following decades saw the sometimes indiscriminate field application of this wide array of materials with predictably uneven results.

A good history of the development and use of stone preservatives in the United Kingdom, particularly in the past thirty years, was written by Bell and Coulthard (1988); Riederer (1972) wrote a similar history of German work. Unfortunately, no such history was found for Italy, where much of the recent experimentation and development of new products and techniques for stone conservation has taken place. But a perusal of the conservation literature reveals that, through the long-term evaluation of the results of early field applications and also through continued trial and error, alkoxysilanes and acrylics have emerged as the preferred conservation materials for stone (Ashurst and Dimes, 1990; Laurenzi Tabasso, 1988a; Lewin and Wheeler, 1985; Weber and Zinsmeister, 1991). Although far from perfect, they have been submitted to extensive testing and characterization and have proven reliable and effective in many practical situations. Epoxies too are widely used for the conservation of stone, but are outside the scope of this study.

1.3 Characteristics of an effective consolidant and/or water repellent for stone

Before discussing the attributes of alkoxysilanes and acrylics, it will be useful to list the attributes which would characterize an ideal consolidant and/or water repellent for stone. Over the past 25 years, a broad consensus has been reached by conservators, researchers, and chemists on the general functions (performance criteria) necessary for an effective stone consolidant. Sleater (1977), Clifton (1984), and Weber and Zinsmeister (1991)

provide comprehensive discussions not only of the performance criteria required of consolidants but of the tests used to evaluate the effectiveness of consolidants in meeting those criteria.

Ideal properties of a consolidant and/or water repellent for stone

- chemical stability, including stability in the presence of ultraviolet (UV) light, to prevent unpredictable alteration (embrittlement or discoloration) of the consolidant by intrinsic or extrinsic factors
- resistance to degradation by acid/alkaline conditions or biological organisms, to prevent destruction of the consolidant in conditions commonly found in external environments
- good depth of penetration (through low viscosity and/or molecular weight), to allow for the deposition of the consolidant throughout the weathered zone and into the sound core of the stone
- moderate vapor pressure and volatility, to prevent reverse migration of the consolidant, to allow for a high percentage of deposition in the stone, and to ensure a reasonable curing time
- high glass transition temperature, to prevent tackiness and increased attraction of dirt and pollutants
- ability to either encapsulate salts or to allow salts to be removed after treatment, particularly important for very fragile or friable salt-laden stone
- reversibility or retreatability

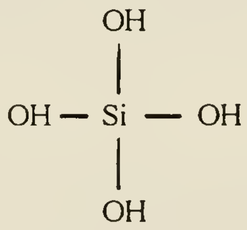
Ideal effects of a consolidant and/or water repellent on the physical and mechanical properties of the treated stone

- no change in color/surface gloss
- no decrease in water vapor permeability
- minimal alteration of pore structure
- significant decrease in water absorption
- increase in strength (compressive, tensile, shear) through improvement of intergranular cohesion and/or readherence of larger grains or flakes
- increase in abrasion resistance
- increase in resistance to salt crystallization
- increase in resistance to freeze-thaw cycling

Unfortunately, no stone preservatives meet all of the ideal characteristics listed above. Indeed, "Is stone preservation by surface application impossible? Probably not, if a suitable material can be found that will achieve adequately deep impregnation, will form a barrier against water movement but not against water vapour, and will not introduce soluble salts into the stonework either directly or as a reaction product" (Ashurst and Dimes, 1990). An evaluation of the effectiveness of a conservation material and an understanding of the appropriateness of its use must be based upon the degree to which it meets the ideal attributes listed above. It must be stressed that no rigid formula exists for the evaluation of the effectiveness of a stone consolidant, nor should it. "A ... logical approach to the evaluation of stone preservatives [for use on a particular stone] is to ascertain the mechanisms of decay, to identify the functions of a treatment intended to counteract those mechanisms, and then to assess the extent to which the treatment is fulfilling those functions" (Arnold and Price, 1976).

1.4 Characterization of alkoxysilanes used for the conservation of stone

Of primary importance in stone conservation are products based on alkoxysilanes. “What make the alkoxysilanes so attractive is the fact that they are unique among the organic monomers which have been employed for stone impregnation in that they are capable (in principle) of being converted from a mobile liquid into a completely stable, inorganic end-product at ambient temperature within the very pores of the stone” (Lewin and Wheeler, 1985). The basic chemistry of alkoxysilanes is as follows:

> These compounds, based on a silicon “backbone” rather than on a carbon one as in organic compounds, can be considered as deriving from silicic acid, better designated as orthosilicic acid:
>
> 
>
> $$\begin{array}{ccc} & OH & \\ & | & \\ OH - & Si & - OH \\ & | & \\ & OH & \end{array}$$
>
> If the hydrogens are replaced by alkyl groups, e.g., methyl ($-CH_3$), ethyl ($-C_2H_5$), etc. (usually designated by -R), the compound is called a silicate ester [or, synonymously, an alkoxysilane] (Charola, 1988).

The generic term alkyl alkoxysilane is used when both alkyl and alkoxy groups are present in the molecule [for example, in a molecule of methyl trimethoxysilane, one methyl group ($-CH_3$) and three methoxy groups ($-OCH_3$) are bonded to the central silicon atom]. By manipulating the type and number of alkyl or alkoxy groups within the molecules, it is possible to produce a variety of polymers with different properties. Properties important to stone conservation include the type of polymerization of the monomers (which affects their reversibility) as well as their elasticity, hydrophobicity, volatility, reactivity, and toxicity. The polymerization of alkoxysilanes occurs through a

reaction sequence of hydrolysis followed by condensation, when alcohol is released as a byproduct (Lewin and Wheeler, 1985). Curing is dependent on the evaporation of the alcohol (Price, 1975), leaving a deposition of amorphous silica within the pores of the stone (Weber and Zinsmeister, 1991).

For a further explanation and clarification of vocabulary, excellent summaries of alkoxysilane chemistry by Charola (1988) and Ashurst and Dimes (1990) are invaluable. Lewin and Wheeler (1985), Marchesini and Bonora (1988), and Koestler and Santoro (1988) also provide good explanations of alkoxysilane chemistry and its relevance to the conservation of stone. From a historical perspective, the development and use of alkoxysilanes for the conservation of stone in the 19th and 20th centuries is best provided by Grissom and Weiss (1981) and in abbreviated forms by Lewin (1988) and Weber and Zinsmeister (1991).

In recent years, alkoxysilanes have been commercially marketed and extensively utilized in the field of stone conservation. Proprietary products encountered in the literature are listed in Table 1.1, with the commercial name, manufacturer, and chemical composition included where known. The products may function as consolidants, water repellents, or both; their primary limitation is that they cannot consolidate grains with a diameter greater than 3 mm, about the size of coarse sand (Wheeler et al., 1991). Generally, these proprietary products consist of one or more of the following:

tetraethoxysilanes: ethyl silicate

silanes[1]:	methyl triethoxysilane (MTEOS) methyl trimethoxysilane (MTMOS) other alkyl alkoxysilane monomers
siloxanes:	methyl phenyl polysiloxane other oligomeric alkyl alkoxysilanes

1.4.1 Ethyl silicates

Ethyl silicates are commonly used to consolidate stone which has lost intergranular cohesion. Initially, it was felt that the chemical similarity of the end-product, amorphous silica, with silicate stones would render it most effective on sandstones. This has largely proven to be true (Wheeler et al., 1991), although in several instances ethyl silicate has been used effectively on limestones and marbles (de Witte et al., 1985; Weber, 1976; Mavrov, 1983; and Torraca, 1988).

The viscosity of ethyl silicate is lower than that of water (Weber and Zinsmeister, 1991), allowing for the good depth of penetration which is of primary importance for an effective consolidant. However, depth of penetration is affected not only by the viscosity and volatility of the consolidant but by the pore structure and permeability of the stone. Because of this, the performance of ethyl silicate is highly variable from stone to stone, but is usually quite good, penetrating at least 5 cm in more permeable sandstones and limestones (Weber, 1985; de Witte et al., 1985) and even up to 10 and 20 cm (Roth, n.d.;

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[1] Silanes are monomers of alkyl alkoxysilanes; oligomers of alkyl alkoxysilanes are sometimes referred to as silanes, but they are technically siloxanes.

Table 1.1 Alkoxysilanes, acrylics, and mixtures: Products and manufacturers in the literature

COMMERCIAL NAME	MANUFACTURER	COMPOSITION	REFERENCE
Ethyl Silicates			
Wacker Stone Strengthener OH	Wacker Chemie	ES	Bradley, 1985
Conservare Stone Strengthener OH	ProSoCo	ES	Zinsmeister, 1988
Tegovakon V	Th. Goldschmidt	ES	de Witte, 1985
Silibond	Stauffer	ES	product literature, 1975
Silanes and Siloxanes			
Brethane	Colebrand	alkyl alkoxysilane	Horie, 1990
Conservare 290	ProSoCo	oligomeric alkyl alkoxysilane	product literature, 1984
Conservare H40	ProSoCo	silane	Koestler, 1988
Dow Corning Z6070	Dow Corning	MTMOS monomer	Rossi-Manaresi, 1985
Dow Corning T4-0149	Dow Corning	MTMOS monomer	Larson, 1982
EP 5850	ICI	MTEOS	Hempel and Moncrieff, 1976
Petrarch M9100	?	MTMOS	Wheeler, 1992
Rhodorsil 11309	Rhone-Poulenc	methyl phenyl polysiloxane	Laurenzi Tabasso, 1985
SS-101	Colcote	MTEOS oligomer	Nishiura, 1984
Silicone Dri-Film 104	General Electric	prepolymerized methyl alkoxysilane	Rossi-Manaresi, 1982
Tegosivin HL 100	Th. Goldschmidt	oligomeric methyl methoxysilane	Laurenzi Tabasso, 1988c
Wacker 290L	Wacker Chemie	oligomeric alkyl alkoxysilane	Laurenzi Tabasso, 1985
Rhodorsil X 54-802	Rhone-Poulenc	MTMOS	Hempel, 1975
Rhodorsil XR-893	Rhone-Poulenc	prepol. methyl phenyl polysiloxane	Rossi-Manaresi, 1976
10336	?	?	Rossi-Manaresi, 1982

Table 1.1 (continued)

COMMERCIAL NAME	MANUFACTURER	COMPOSITION	REFERENCE
Acrylics			
Acryloid B67	Rohm and Haas	BMA	Gale, 1982
Acryloid B72	Rohm and Haas	EMA/MA copolymer	Wheeler, 1991
Paraloid B72	Rohm and Haas	EMA/MA copolymer	Horie, 1990
Raccanello E0021	Racanello	acrylic	Larson, 1982
Safe Stone	Sinco Mec Kolor	MMA/BMA copolymer	Rossi-Manaresi, 1985
Alkoxysilane Mixtures			
Conservare Stone Strengthener H	ProSoCo	ES/MTEOS	Zinsmeister, 1988
Geviciet	?	ES/MTEOS	de Witte, 1985
Tegovakon T	Th. Goldschmidt	ES/MTEOS	Hempel, 1975
Wacker Stone Strengthener II	Wacker Chemie	ES/MTEOS	de Witte, 1985
Wacker VP 1301	Wacker Chemie	ES/ETEOS	Larson, 1982
Acrylic/alkoxysilane mixtures			
Product 460	Mased	silconate/acrylic copolymer	Rossi-Manaresi, 1976
E 55050, formerly E 0057	Raccanello	acrylic/alkoxysilane mixture	Charola, 1982; Hanna, 1984
Nonfarmale custom mixture	none	EMA/MA copolymer and prepolymerized methyl alkoxysilane mixture	Nonfarmale, 1976

Abbreviations:

BMA = butyl methacrylate
EMA = ethyl methacrylate
ES = tetra-ethoxysilane
ETEOS = ethyl triethoxysilane
MA = methyl acrylate
MMA = methyl methacrylate
MTEOS = methyl triethoxysilane
MTMOS = methyl trimethoxysilane

Weber, 1976); it is considerably less effective in more compact stones (Weber, 1976).

Temperature has little effect on the curing of the polymer but higher humidities tend to accelerate the polymerization of the ethyl silicate (Mavrov, 1983). As curing proceeds, the ethyl silicate polymer is not precipitated as a continuous film, but as isolated accumulations with different form, size, and structure; after hardening the polymer may exhibit holes, tears, cracks and non-compensated internal strains (Mavrov, 1983; Stambolov and van Asperen de Boer, 1976). In a study of three limestones treated with ethyl silicate, it was found that the polymer was deposited within pores but not on pore walls: "Not finding a suitable surface to interact with - as these are limestones - the ethyl silicate reacts with itself forming these apparently discrete masses [within the pores of the stone]" (de Witte et al., 1985). In a comparative study conducted on sandy limestones, ethyl silicate showed worse contact with the stone surface than methyl trimethoxysilane and did not form bridges between grains or pore walls (Mavrov, 1983).

The results of experiments which measure physical changes in the stones treated with ethyl silicate are variable. All agree that ethyl silicate causes very little change in the color and reflectance of most stones, and that it forms no deleterious byproducts, such as soluble or insoluble salts, which might discolor or further harm the stone (Zinsmeister et al., 1988; de Witte et al., 1985; Torraca, 1988). Measurements of reductions in the porosity of treated stones range from 2% to 10% (Zinsmeister et al., 1988; Weber and Zinsmeister, 1991), and water vapor permeability may be reduced by up to 50% (Weber, 1985). Generally, the water absorption rates of stones are not much affected by treatment with ethyl silicate, which is predictable because ethyl silicate has no hydrophobic properties. De Witte et al. (1985) record a decrease in capillary absorption of 90% in a limestone treated with ethyl silicate, but note that the effect disappeared after one month

(presumably after cure).

The effects of ethyl silicate on the mechanical properties of treated sandstones are quite good. Compressive strength frequently increases by 50 - 100%, and similar increases in modulus of rupture and abrasion resistance are standard (Zinsmeister et al., 1988; Weber and Zinsmeister, 1991; Laurenzi Tabasso and Santamaria, 1985). However, ethyl silicate does not have the adhesive properties necessary to bridge large voids, reattach larger grains to each other, or adhere loose flakes (Nishiura, 1987; Rossi-Manaresi, 1976).

Aging tests reveal significant decreases in the efficiency of ethyl silicate after ten years; however, retreatment is possible and has good results (Sattler and Snethlage, 1988). Ethyl silicate is also highly UV-resistant due to its SiO_2-like structure (Weber, 1976), although a slight discoloration has been noted after prolonged exposure to artificial UV and salt weathering (Laurenzi Tabasso and Santamaria, 1985). The susceptibility of ethyl silicate to biodeterioration varies according to the commercial product used: in one comparative study, Tegovakon V had excellent resistance, while Conservare OH showed only moderate resistance. This variation is probably a function of additives or contaminants peculiar to each commercial product (Koestler and Santoro, 1988). Ethyl silicate cannot effectively block or encapsulate hygroscopic sodium sulfate salts (Na_2SO_4) already present in the stone (Mavrov, 1983). The cycling of these salts in the presence of moisture will eventually counteract any consolidative effects and advance the deterioration of the treated stone, but alternatively it is possible to remove the salts after consolidation. Treatments with ethyl silicate are not reversible.

1.4.2 Silanes and siloxanes

Silanes and siloxanes are employed in stone conservation for their moderate consolidating abilities and excellent water-repellency. "The end product of their hydrolysis and condensation reactions contains hydrocarbon groups attached to the silicon or siloxane backbone, and these present a non-polar aspect to the surroundings, which inhibits the entry of liquid water into the stone" (Lewin, 1988). Thus silanes and siloxanes do not seal the surface of the stone but allow the passage of water vapor from the interior of the stone, preventing any harmful accumulation of water and/or salts behind the treated surface.

Much of the early testing and use of silanes was conducted at the Victoria and Albert Museum in Great Britain by Hempel and Moncrieff (1976); they primarily experimented with and used a monomer of methyl trimethoxysilane (X 54-802) for the consolidation of carbonate stones and, to a lesser extent, sandstones (Table 1.1). Extensive characterization of the silane was performed by Moncrieff (1976), who found that it had excellent UV and chemical stability, and a hardness and thermal expansion coefficient similar to that of calcite. The silane was not brittle but was not flexible either; depth of penetration was moderate, ranging from 5 cm in weathered marble to no penetration in sandstone, and seemed to be a function of the permeability of the stone. No conclusive results were obtained from porosity and permeability tests, nor were any tests of mechanical strength conducted. Treatments applied to all stones were non-reversible.

In recent years, the two most commonly used silanes and siloxanes have been a monomer of methyl trimethoxysilane (MTMOS), marketed as Dow Corning Z6070 or Dow Corning T4-0149, and a prepolymerized methyl alkoxysilane, marketed as Silicone Dri-

Film 104 (Table 1.1). The significant difference between these two products is that the MTMOS monomer reacts to form a network polymer, making it non-reversible, while Dri-Film reacts to form linear chain polymers, making it reversible (Gnudi et al., 1981; Charola et al., 1984a). As well, scanning electron microscopy (SEM) shows that MTMOS forms an extremely thin but relatively continuous film on stone samples, while Dri-Film 104 forms a somewhat thicker but less continuous film (Rossi-Manaresi and Tucci, 1985). Both of these products are now used without catalysts to aid in curing; catalysts were found to be unpredictable and unstable, and to cause a darkening of the stone. As well, attempts to retreat surfaces previously treated with a catalyst caused swelling of the old resin and disruption of the stone (Larson, 1982). Although loss to evaporation is considerably increased and the consolidative effect reduced, these considerations are outweighed by the possibilities of retreatment and the minimal alteration in the appearance of the stone (Larson, 1982; Bradley, 1985).

Silanes and siloxanes have a viscosity lower than water, allowing for good penetration into permeable stone. Temperature has little effect on the curing of the polymer, but humidity does: as humidity increases, the rate of polymerization accelerates (Mavrov, 1983; Charola et al., 1984b). As with ethyl silicate, silanes and siloxanes do not form continuous films, but form isolated accumulations with different form, size, and structure; after hardening they exhibit holes, tears, cracks, and non-compensated internal strains (Mavrov, 1983; Stambolov and van Asperen de Boer, 1976). In contrast, another study revealed that such defects disappeared in MTMOS films which polymerized at a relative humidity of 33%, while "nearly perfectly glasses" were formed at 11% relative humidity; however, much more of the silane was lost to evaporation at the lower humidities (Charola et al., 1984b).

The degree of water-repellency imparted is also dependent on the type of stone to which the silane or siloxane is applied. It is consistent and good on fine-grained sandstones but can be variable within a single stone, especially in the case of coarse-grained or inhomogeneous sandstones (Wendler and Snethlage, 1988). When the treatment is uniformly deposited, water repellency is 95 - 100 % (Weber, 1976); this new hydrophobicity of the treated stone also makes the effects of freeze-thaw cycling negligible (Nishiura et al., 1984). The porosity of stones are little affected by impregnation with MTMOS (Nishiura et al., 1984), but silanes may reduce water vapor permeability by 5 - 8% (Weber and Zinsmeister, 1991).

To test its consolidative effects on different types of materials, Charola et al. (1984b) attempted to consolidate powdered fine silica, coarse silica, and marble dust with MTMOS and found that :

> Superior consolidation was achieved for fine silica for which MTMOS has a chemical affinity. The coarse silica was not as well consolidated as the fine silica due possibly to the larger intergranular spaces in the sample. Almost no consolidation was achieved for the marble powder... Empirical evidence exists, however, for the consolidation of marble and limestone with MTMOS... The consolidation might involve a physical 'locking-in' of loose grains with a network of polymer rather than a chemical bridging between grains.

Mavrov (1983) also says that the compressive strength MTMOS imparted to a sandy limestone was equal to that imparted by ethyl silicate. Laurenzi Tabasso too states that "a good consolidating effect is given by alkyl alkoxysilanes" but does not quantify or reference that statement (1988a). In contrast, others state that alkoxysilanes are not useful as consolidation materials, and others simply note that they are poor adhesives (Rossi-Manaresi and Tucci, 1985; Weber and Zinsmeister, 1991; Stambolov and van Asperen de Boer, 1976). But another study showed that MTMOS does form polymer bridges within

the pores of the stone, which may give it some adhesive strength (Mavrov, 1983). Because the results of the studies found in the literature were so inconsistent, the changes wrought in the mechanical properties of stones after treatment with silanes are assumed to be considerably dependent on the properties of the stone itself.

Like ethyl silicate, silane and siloxane resins are highly UV-resistant due to their SiO_2-like structure (Weber, 1976); this chemical composition also makes them resistant to attack by biological organisms. However, MTMOS ages more quickly than non-hydrophobic consolidants like ethyl silicate under the action of sulfuric acid, "which attacks blocked functional groups left in the polymer." MTMOS cannot effectively block or encapsulate hygroscopic Na_2SO_4 salts already present in the stone (Mavrov, 1983), but again this allows for their removal after treatment. Estimates of the durability of silanes and siloxanes range from 4 to 10 years (Stambolov and van Asperen de Boer, 1976; Wendler and Snethlage, 1988; Moncrieff, 1976; Bell and Coulthard, 1988). The wide range in the durability of the hydrophobing treatments is affected by many variables, including the type of stone treated, the method of application, and the micro- and macro-climate. Retreatment is feasible because of the chemical stability of the uncatalysed silanes and siloxanes; no swelling is caused by the application of solvents or by the reapplication of silane (Moncrieff, 1976).

1.4.3 Ethyl silicate/silane mixtures

Mixtures of ethyl silicates and silanes are frequently employed in stone conservation, and have been used most extensively in Germany beginning in 1965 (Riederer, 1972). They can impart both intergranular cohesion and water-repellency in a single application. The most widely-used mixtures are combinations of ethyl silicate and methyl triethoxysilane

(MTEOS), which are sold commercially in Europe and in North America as Wacker Stone Strengthener H and Conservare Stone Strengthener H respectively (Table 1.1). For clarity, these mixtures will hereafter be referred to as H mixtures.

Weber (1985) found the depth of penetration of ethyl silicate/silane mixtures (about 20 mm) to be less than that of ethyl silicate (about 50 mm) when applied to the same sandstone. Water vapor permeability may be reduced by 15 - 50% (Weber and Zinsmeister, 1991; Laurenzi Tabasso et al., 1988c). The application of ethyl silicate/silane mixture causes no color change (de Witte, 1985). Other changes in the physical, mechanical, and aging properties of stones treated with mixtures of ethyl silicates and silanes are similar to those caused by ethyl silicate alone. The important exception is the increase in water-repellency: this protects stone by reducing or eliminating cycles of salt crystallization and freeze-thaw. The resistance of H mixtures to biodeterioration is also greater than that of ethyl silicate alone (Koestler and Santoro, 1988).

1.5 Characterization of acrylics used for the conservation of stone

The majority of acrylic polymers used in stone conservation are made from methacrylate monomers, which are derived from methacrylic acid. The chemistry of acrylic resins is similar to that of alkoxysilanes, with manipulations of the alkyl (-R) group in the monomer used to produce a range of polymers, such as methyl methacrylate and butyl methacrylate (Table 1.1) (Horie, 1990). In practical application, acrylic oligomers or polymers are diluted in volatile solvents and applied to the stone, with polymerization occuring upon evaporation of the solvent. In the field of stone conservation, acrylics are commonly used as adhesives to reattach both larger grains and detached layers of stone.

At very low concentrations acrylics are also employed as consolidants to reestablish the intergranular cohesion of the stone, and increases in compressive strength are similar to those imparted by ethyl silicate (Laurenzi Tabasso and Santamaria, 1985). In this way the function of an acrylic overlaps with the function of ethyl silicate but with the added capabilities of bridging larger gaps and adhering larger grains (Rossi-Manaresi and Tucci, 1985). Although not as effective or long-lasting as silanes and siloxanes, acrylics are also inherently water-repellent, and this property is also exploited in stone conservation (Charola et al., 1985; Rossi-Manaresi and Tucci, 1985; Laurenzi Tabasso and Santamaria, 1985).

Ethyl methacrylate (EMA), methyl methacrylate (MMA), butyl methacrylate (BMA), polymethyl methacrylate (PMMA), and polybutyl methacrylate (PBMA) have all been used extensively in the field of conservation. But in recent years the use of Paraloid or Acryloid B72 (the same product, manufactured by Rohm and Haas, but sold as Paraloid in Europe and as Acryloid in North America) has predominated. It is an ethyl methacrylate/methyl acrylate copolymer with a molar ratio of 70:30 (Horie, 1990); for simplicity, this copolymer is hereafter referred to as MMA rather than EMA/MA. The properties of this copolymer are well-known, for it has been extensively tested in laboratory situations and applied in the field.

Because the acrylic molecules are large, MMA must always be applied in very dilute solutions of organic solvents (Stambolov and van Asperen de Boer, 1976), with toluene and xylenes used most commonly (Horie, 1990). The viscosity and volatility of the solvent, the pore structure of the stone, and the drying conditions after impregnation greatly affect the depth of penetration and the quantity of acrylic deposited in the stone (Domaslowski, 1987-88). The high volatility of the organic solvents normally used to

make acrylic solutions results in the significant evaporation of material before polymerization and may cause the reverse migration of the acrylic, resulting in a nonuniform deposition. Migration is reduced when solvents of very low volatility are used (e.g., diethyl benzene), or if slow, long-term drying is allowed (Domaslowski, 1987-88). Long-term drying can be achieved by placing the treated object in a vapor-saturated atmosphere, but this method is not normally practicable for large architectural surfaces (Hansen et al., 1993). Although good depths of penetration in marble and tuff have been reported using an unspecified solvent (Laurenzi Tabasso et al., 1988b and 1988c), in general, practical depths of impregnation are only a few millimeters in from the surface, giving MMA relatively poor penetration for stone consolidation (Horie, 1990; Rossi-Manaresi and Tucci, 1985).

Attempts to characterize the effects of MMA on the porosity and water repellency of treated stones are far from conclusive. In one study of a porous tuff it was found that MMA affected porosity only minimally and that it imparted almost no water repellency, thus offering no increase in resistance to freeze-thaw cycles (Nishiura et al., 1984). But a second study of tuff and marble showed that porosity was decreased and that water absorption was reduced by significant amounts (Laurenzi Tabasso et al., 1988b). This variation may be a result of the use of different concentrations of MMA in different solvents, differences in the stone substrate to which they were applied, and the length of time allowed for cure before testing.

In a comparative study of marble and tuff samples treated with MMA in an unspecified solvent or an H mixture, treatments with MMA caused about a 50% reduction in vapor permeability from untreated samples, while the reductions caused by the H mixture were slightly greater and therefore worse. In the same study, samples treated with MMA also

exhibited a greater increase in compressive strength (about 100%) and a better depth of penetration (Laurenzi Tabasso et al., 1988b and 1988c). Weber and Zinsmeister (1991) estimate a lower reduction in water vapor permeability in stone treated with MMA dissolved in hydrocarbons, about 15 - 30 %.

Treatments with MMA cause an initial discoloration of the stone which has been shown to alter further after prolonged exposure to UV radiation and acid fog cycling (Laurenzi Tabasso and Santamaria, 1985; Laurenzi Tabasso et al., 1988b and 1988c). But in general, MMA is stable and effective for up to 10 years of external exposure in temperate climates (Torraca, 1988) and exhibits good UV stability and resistance to acidic atmospheric pollutants (Charola et al., 1985; Weber and Zinsmeister, 1991; Tucci et al., 1985). In particular, Paraloid (or Acryloid) B72 does not become insoluble or degrade significantly in normal conditions of exposure, although oxidation and other changes do occur slowly, and it is listed as a Feller Class A material (Horie, 1990). Thus, although theoretically reversible in organic solvents (Munnikendam, 1967), it is sometimes difficult to induce the reverse migration of MMA and remove it completely from the treated stone. MMA exhibits moderate resistance to biodeterioration, about the same as that of the Conservare H mixture and better than that of ethyl silicate alone (Koestler and Santoro, 1988), possibly because it is not used as a carbon source by fungi (Nugari and Priori, 1985). Like ethyl silicate, silanes, and siloxanes, MMA is not effective at immobilizing salts (Arnold and Price, 1976).

1.6 Characterization and use of alkoxysilane/acrylic mixtures for the conservation of stone

In 1976, Ottorino Nonfarmale reported the successful treatment of the sandstone tomb of

Francisco Coriolani in the cloister of San Domenico, Bologna, using a mixture of an alkyl alkoxysilane (Silicone Dri-Film 104, a prepolymerized methyl alkoxysilane) and an acrylic (Paraloid B72, an ethyl methacrylate/methyl acrylate copolymer).[2] The development of the mixture was based on the idea that the adhesive properties of the acrylic resin, when combined with the water-repellent properties of the alkyl alkoxysilane, would not only permit the attachment of raised crusts and the consolidation of the stone which had lost cohesion, but would also prevent the future deterioration of the stone by imparting water-repellency. A depth of penetration of greater than 4.5 cm was achieved; tests of the treated stone, in comparison with untreated samples, showed a decrease in porosity of 14.8%, a decrease in the water absorption coefficient of 99.7%, an increase in compressive strength of 68%, and an increased resistance to attack by sulfuric acid (Nonfarmale, 1976). A survey of the facade eight years after treatment revealed no new deterioration of the stone (Rossi-Manaresi, 1982).

Since that first report, conservators have frequently employed mixtures of acrylics and silanes, both independently-formulated and proprietary, on all types of stone:

- A number of sandstone buildings and monuments in Bologna were treated with a variety of conservation materials; treatments with either a mixture of MMA and a prepolymerized methyl alkoxysilane (Silicone Dri-Film 104) or a monomer of MTMOS produced the best consolidative and water repellent effect (Rossi-Manaresi, 1976).

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[2] The exact formulation of this mixture was: 10% of a 30% solution of Paraloid B72 in 1:1 xylenes and toluene; 10% of a 70% solution of Silicone Dri-Film 104 in an organic solvent; and 80% of 1,1,1-trichloroethane (Nonfarmale, 1976).

- Samples of a porous tuff from Matera, Italy, were treated with a range of consolidants, with the best consolidative and water-repellent effects imparted by a mixture of MMA and an alkyl alkoxysilane, a siloxane, and a silicone resin of unspecified nature (Cuttano et al., 1981).

- Limestone and marble sculptures by Jacopo della Quercia on the facade of San Petronio, Bologna, had formed surface crusts beneath which the stone was very friable. The sculptures were preconsolidated and later consolidated by brush-applying a mixture of MMA and a prepolymerized methyl alkoxysilane (Silicone Dri-Film 104). It was possible to clean heavy deposits of dirt from the surfaces after preconsolidation (Gnudi et al., 1981).

- Carrara marble and English limestone and sandstone sculptures at the Victoria and Albert Museum were treated with a mixture of MMA and MTMOS. The mixture allowed for preconsolidation of friable areas, deep consolidation, cleaning and salt extraction after consolidation, and retreatment with no harmful effects (Larson, 1982).

- Salt-laden Egyptian limestone reliefs were consolidated by mixing pure MTMOS and a commercial acrylic/alkoxysilane mixture (Raccanello E55050) and drip-feeding it onto the surface of the stone. It was possible to extract salts from the stone after consolidation of the fragile surfaces (Hanna, 1984).

- A friable and salt-laden oolitic limestone sculpture was consolidated by drip-feeding and brushing a mixture of 1% MMA in uncatalyzed MTMOS (Larson and Dinsmore, 1984).

Only one example of the use of a mixture of ethyl silicate and MMA was found in the literature: Andersson (1985) reported the use of MMA dissolved directly in ethyl silicate and applied to sandstone in Sweden with apparently good results. Because of its limited use, this mixture will not be considered in the following discussion.

A number of comparative studies have been published in which acrylic/alkyl alkoxysilane mixtures are tested alongside most other materials used for the conservation of stone (Appendix A). The effectiveness of custom mixtures, based upon the consolidative and water repellent effects which they impart to all types of stones, almost always exceeds that of epoxies, alkaline silicates, hydroxides, and proprietary acrylic/silane mixtures (Cuttano et al., 1981; Rossi-Manaresi, 1976), therefore comparisons with these materials will not be considered in this review. But the effectiveness of acrylic/silane mixtures varies in relation to that of ethyl silicates, acrylics, and alkyl alkoxysilanes used alone, and of proprietary H mixtures (Cuttano et al., 1981); therefore attention will be devoted to the performance of custom mixtures of MMA dissolved in MTMOS or Dri-Film 104 in comparison with the latter group. The test results summarized in the following sections have been culled from many different comparative studies conducted on many different types of stone, and are intended to provide only a general idea of the performance of mixtures in relation to other conservation materials. The results of all experimental programs are highly influenced by the physical condition and chemical nature of the stone to which they are applied, and may vary accordingly.

1.6.1 Properties of MMA/alkyl alkoxysilane mixtures

Studies show that mixtures of MMA/alkyl alkoxysilanes penetrate deeply and

homogeneously into stone (Cuttano et al, 1981; Charola et al, 1982). The addition of up to 5% MMA (which has large molecules and generally poor depth of penetration) to MTMOS or Dri-Film 104 (which have low viscosity and good depth of penetration) does not alter the depth of penetration of the latter (Charola et al., 1984a). The depth of penetration of a mixture of MMA/Dri-Film 104 in sandstone samples was found to be good and homogeneous, equal to that of MTMOS alone and equalling or bettering that of proprietary H mixtures. However, applications of the same materials in the field gave different results: the MMA/Dri-Film and the H mixtures had the greatest depths of penetration while that of MTMOS alone was entirely superficial (Rossi-Manaresi, 1976). Another study indicated that the H mixture had the best depth of penetration (15 cm) in a porous tuff, but that of an MMA/Dri-Film mixture was also good (10 cm) (Cuttano et al., 1981).

1.6.2 Physical changes in stone caused by mixtures of MMA/alkyl alkoxysilane

The addition of MMA to alkyl alkoxysilanes can cause discoloration and a patchy appearance in stone (Bradley, 1985). This change in the appearance of treated stones is usually attributed to the discoloring effects of MMA, but one study showed that both a mixture of MMA/Dri-Film and MTMOS alone darkened sandstones (Rossi-Manaresi, 1976).

The water absorption coefficients of stones after treatment with mixtures of MMA/Dri-Film 104 are consistently reduced by 90 - 100%. Quite similar reductions in water permeability are imparted by MTMOS alone and proprietary H mixtures (Rossi-Manaresi, 1976; Cuttano et al., 1981). Measurements of porosity reductions in treated stones are

quite variable because these figures are greatly influenced by the physical characteristics of the original stone. For instance, one study showed no reduction in the porosity of stone treated with MTMOS monomer, whereas a mixture of 2% MMA in MTMOS caused a 20% decrease; ethyl silicate and H mixtures caused a 25% decrease (Bradley, 1985). In contrast, a stone treated with MTMOS alone showed a decrease in porosity of 21%, while mixtures of MMA/Dri-Film 104 and H caused only about a 15% decrease (Rossi-Manaresi, 1976)

1.6.3 Mechanical changes in stone caused by mixtures of MMA/alkyl alkoxysilane

The application of a mixture of MMA and MTMOS provides excellent increases in the mechanical properties of deteriorated stone. Moreover, the strength imparted by the combination of the two materials is greater than that imparted by either one alone (Bradley, 1985). A mixture of MMA and an MTEOS oligomer was found to give excellent consolidation to fragments of crushed stone 1- 4 mm in diameter; the mixture proved more durable than either the silane or the MMA alone after exposure to a series of abrasion and freeze-thaw cycles (Nishiura, 1987). Similarly, an MMA/Dri-Film 104 mixture gave the highest increase in compressive strength in weathered sandstone, higher than that of MTMOS alone or proprietary H mixtures (Rossi-Manaresi, 1976)

1.6.4 Aging of mixtures of MMA/alkyl alkoxysilane and their effects on the aging of stone

Acrylic/silane mixtures are highly stable in the presence of UV radiation; extensive exposure to UV radiation causes no change in the morphology of a mixture of MMA and

Dri-Film (Tucci et al., 1985) or in its color (Gnudi et al., 1981). The increased resistance to destruction by salt crystallization imparted by MMA/MTMOS mixtures is also quite good: stone samples treated with MMA/Dri-Film 104 mixtures had excellent resistance to salt crystallization, better than an H mixture (Cuttano et al., 1981). In another study, a mixture of MMA/Dri-Film 104 gave the greatest increase in resistance to salt cycling; treatments with MTMOS gave good results and H mixtures of ethyl silicate/MTEOS gave lesser but also good resistance (Rossi-Manaresi, 1976). Because mixtures do not encapsulate salts, it is easy to preconsolidate fragile surfaces with the mixture and then remove salts (Hanna, 1984; Bradley, 1985). Cleaning and removing dirt and encrustations from stone surfaces is also possible after treatment with a mixture of MMA/Dri-Film 104 (Gnudi et al., 1981).

Because MTMOS forms network polymers, mixtures of MMA and MTMOS are not reversible. In contrast, Silicone Dri-Film 104 forms linear chain polymers, and mixtures of MMA/Dri-Film 104 can remain soluble in organic solvents for at least four years after polymerization (Gnudi et al., 1981). In an interesting study, a mixture of MMA/Dri-Film 104 was exposed to a sulfuric acid fog; results revealed that the mixture was not degraded by acid but rather that acid caused *in situ* polymerization of the silicone resin. This process proceeded "via the remaining alkoxy groups which [were] still present in the pre-polymerized product," the presence of which had been previously demonstrated by infra-red (IR) analysis. This continuation of polymerization leads to a tri-dimensional network of resin (as opposed to the original linear chain polymers formed in the initial reaction) which serves to hold the grains of stone in place (Tucci et al., 1985). It is important to note that if extensive networking does take place, MMA/Dri-Film 104 mixtures would no longer be reversible.

1.6.5 Effects of mixtures on physical, mechanical, and chemical properties of acrylics and silanes

Despite the extensive use of acrylic/silane mixtures, their physical, mechanical, and chemical interactions were little understood until recently. In particular, the short- and long-term effects of the acrylic on the polymerization of the silane were unknown. But an important study of MMA/MTMOS mixtures conducted by Wheeler et al. (1991) has provided an increased understanding of their interaction. The results of that study are outlined below:

> - The viscosity of a mixture of 5% MMA in MTMOS is almost five times greater than that of the MTMOS monomer alone; however, the viscosity of the mixture is still close to that of water and is considered low enough to allow for sufficient depth of penetration and thus effective consolidation of stone.
>
> - The addition of MMA does not reduce the vapor pressure of MTMOS and thus is not effective in controlling evaporative loss of MTMOS during early stages of polymerization.
>
> - At later stages of polymerization, a 2% increase in mass retention of the mixture is achieved for every 5% of MMA added to MTMOS. The MMA causes "entrapment" of the MTMOS in the stone, allowing *in situ* reactions to take place.
>
> - Hydrolysis and condensation of MTMOS are dramatically slowed by the addition of MMA. "The slowing of the reaction is probably due to the fact that water cannot as easily hydrolyze the MTMOS and its oligomers due to the added

hydrophobicity imparted to the solution by [MMA]." However, once a gel is formed, MMA appears to promote condensation reactions in the MTMOS.

- The modulus of rupture (MOR) of sandstone was improved by 74% after treatment with MTMOS alone, while a solution of 10% MMA in toluene increased the MOR by 100%. A mixture of 1% w/v MMA in MTMOS increased the modulus of rupture by 124% and the increase from a mixture of 10% B72 in MTMOS exceeded the measuring capacity of the instrument.

- Solutions of MMA in toluene proved as effective or more so at consolidating an oolitic Indiana limestone.

1.7 Conclusions

When applied as a mixture, methyl methacrylate (MMA) and methyl trimethoxysilane (MTMOS) satisfy many of the requirements of an ideal consolidant and water repellent for stone. The adhesive and consolidative abilities of MMA, combined with the water repellent and consolidative properties of MTMOS, result in greater strength and better resistance to weathering agents such as water and salts. In general, these mixtures perform better than ethyl silicate or mixtures of ethyl silcate and silanes, and better than acrylics or silanes alone. Mixtures of MMA and MTMOS can be considered one of the most effective treatments for the conservation of stone currently available.

However, MMA and MTMOS do interact with each other during polymerization, and thus affect the manner and extent to which a treated stone is preserved. No comparative studies or treatment reports were found on the effects or effectiveness, if any, of applying

the acrylic and the silane to stone in a series of steps as opposed to a single mixture. A sequential application is more time-consuming than the one-step mixed application, but what if the condition of the stone made the former method of treatment more desirable? What would be the other drawbacks or benefits resulting from the separate application of the elements of the mixture? The following questions arose:

- Would the independent application of the silane allow for greater depth of penetration, resulting in the greater water repellency and increased resistance to salt crystallization of the treated stone? Or would the prior application of the acrylic inhibit the penetration of the silane, thus decreasing its efficiency?

- Because the acrylic is reversible and soluble in the silane, would the application of the silane over the cured acrylic cause its extensive resolubilization and redistribution within the stone? If so, would this be a positive or negative effect?

- How would the water vapor transmission rates of the stone be affected by sequential versus mixed applications of acrylic and silane?

- Would the color change in the stone be reduced or altered if the acrylic and silane were applied in a sequence rather than a mixture?

- If the acrylic were resolubilized by the silane, would the acrylic still "entrap" the silane in the late stages of its polymerization (resulting in a greater retention of consolidative materials in the stone, thus an increase in the efficacy of the treatment) if the materials were applied in a sequence rather than a mixture?

The experimental program which follows was designed to begin to answer some of these questions, and to compare the differences, if any, caused by consecutive and mixed applications of alkyl alkoxysilanes and acrylics on the physical and mechanical properties of stone.

Chapter 2. Experimental Program

2.1 Overview

Stone samples from the convento column at Mission San José y San Miguel de Aguayo were petrographically and mineralogically analyzed using polarized light microscopy and x-ray diffractometry, and the stone was determined to be an impure limestone containing a high percentage of quartz sand. These results, combined with the analysis of deterioration mechanisms affecting the column and widely-recognized criteria for effective stone consolidants, guided the selection of conservation materials for the stone. The use of mixtures of these materials was well documented in the conservation literature, while the use of these materials in sequential application was not. However, because of the localized deterioration of the column and the need to infill large areas of loss after consolidation, the use of the materials in a sequence was more desirable than their use in a mixture. To determine if a sequence would be as effective as a mixture, a pretreatment experimental program was designed to evaluate any physical and mechanical differences in treated stone caused by the two methods of application.

For pretreatment testing, it was necessary to use artificial facsimiles. It was not possible to obtain weathered samples from the column itself due to its small size, visibility, and structural importance. As an initial substitute, samples of a visually similar, unweathered local limestone were cut into two-inch cubes and sent to the Architectural Conservation Laboratory (ACL) at the University of Pennsylvania by San Antonio Missions National Historical Park. To approximate the existing condition of deteriorated sections of the

column stone and to allow for measurable treatment results, the samples were subjected to accelerated weathering using baths of sodium sulfate, sulfuric acid, and hydrochloric acid; however, because of the low permeability of the stone, the samples could not be sufficiently weathered in the given time (two months). Thus artificial facsimiles, rather than stone samples, were used in the experimental program. Composed of marble dust, quartz sand, and water, they were formulated to serve as simple analogs of the column stone.

It must be emphasized that the facsimiles were in no way intended to replicate the chemical or physical properties of the limestone, and the quantitative results of the experimental program cannot be inferred to correlate to the column stone. But certain advantages are derived from treating and testing the facsimiles rather than the stone samples. Because the same treatments were applied to all of the facsimiles, the method of their application was the only variable. Thus the primary purpose of the experimental program was not to measure the effectiveness of the individual treatments in consolidating the substrate but to measure the effects of the treatments on each other, which thereby influenced their effectiveness in consolidating the substrate. Because the facsimiles were more uniform in composition than the stone samples, variations in the test results of different treatment groups could be assumed to be caused by the interaction of the treatments with each other rather than by inconsistencies in the substrate; the uniformity of the facsimiles also allowed for more statistically comparable test results. Because the facsimiles were inherently weak, measurable test results could be obtained, which was not possible with the impermeable, unweathered stone samples. Thus, although the quantitative results of the experimental program cannot be applied to the column, qualitative comparisons of the relative effectiveness of the two methods of application, as a result of their interaction, can be made. The information derived from these

comparisons is valid not only for the specific instance of the limestone column but for the general conservation of stone.

After manufacture, the facsimiles were first treated with ethyl silicate; subsequently, a methyl acrylate/ethyl methacrylate copolymer (MMA) and a methyl trimethoxysilane monomer (MTMOS) were applied either in sequence or in mixture. Tests were selected to measure the physical and mechanical properties of the facsimiles after treatment, and were based on standardized procedures whenever possible. These tests measured the depth of penetration and the microstructure of sequences and mixtures of MMA and MTMOS, as well as changes in color, water absorption, bulk specific gravity, water vapor permeability, and resistance to salt crystallization of the individual facsimiles.

The results of the experimental program revealed several significant differences between untreated facsimiles, facsimiles treated with sequences, and facsimiles treated with mixtures. A comparison between untreated and treated groups revealed that both methods of treatment caused a slight change in color and a decrease in water vapor transmission rates, but greatly reduced water absorption rates and increased resistance to salt crystallization. A comparison between the two methods of treatment revealed that the mixture of MMA and MTMOS exhibited a greater mean depth of penetration than the sequence, that the microstructures of the two treatment methods differed, and that facsimiles treated with a mixture exhibited a greater mean increase in bulk specific gravity than facsimiles treated with a sequence. No significant differences in color change, water absorption, water vapor transmission, or resistance to salt crystallization existed between the sequential and mixed treatment methods. Based upon these results, the effectiveness of a combined application of MMA and MTMOS was felt to be slightly better than that of a sequential application. These conclusions were then considered in combination with the

specific deterioration patterns and other treatment requirements of the convento column stone in order to determine the most effective conservation treatment.

2.2 Characterization of the convento column stone

The stone of the column in the convento of Mission San José y San Miguel de Aguayo, San Antonio Missions National Historical Park, Texas, was characterized in order to determine stone composition and type, to identify relevant physical and mechanical properties of the stone, to gain an understanding of the deterioration mechanisms affecting the stone, and to determine the broad categories of treatments required to remedy the deterioration. Only after establishing these variables could appropriate conservation materials be selected and an experimental program be designed to further evaluate and refine the conservation treatments.

Two separate mineralogic and petrographic analyses were conducted on samples taken from the column. In 1988, Masonry Stabilization Services Corporation (MSSC) analyzed samples of stone and white patching material from the column (Gale, 1988). The stone was characterized as an impure limestone and the patching material as gypsum. The results of microscopic examination and the interpretation of x-ray diffraction patterns were as follows:

> Under the microscope, the stone appears to be a limestone containing an appreciable amount of impurities: most of the grains appear to be carbonate and are imbedded in a very fine-grained matrix of iron-bearing material. The patch is fine-grained and circular voids were observed, suggesting a cast material such as gypsum.
>
> The x-ray diffraction patterns showed the stone is an impure limestone containing significant [amounts] of goethite (hydrated iron oxide) and clay minerals. A trace of feldspar is also present along with quartz.

> The patch is gypsum (hydrated calcium sulfate) with only a trace of impurities present. One would not expect this material to be suitable as a patch for exterior usage (Gale, 1988).

In the same report, the stone sample was analyzed for anionic salt content, pH, and solubility. Tests found no chlorides (Cl^-) and nitrates (NO_3^-) in only 0.5 ppm, whereas sulfates (SO_4^{--}) occurred in 240.0 ppm. The pH of the stone sample was 7.21. The water soluble content (%/sample wt.) was 0.5%, and the acid soluble content was 48.85%, reflecting of the high proportion of calcium carbonate in the stone (Gale, 1988).

Although the high sulfate content may derive in part from the mineralogical composition of the stone, its most likely source is the white bedding and patching mortar previously used on the column, which was identified as gypsum. Gypsum (hydrated calcium sulfate) is water soluble; upon exposure to exterior weathering conditions such as rain and snowmelt, the gypsum can move into solution as SO_4^{2-} and permeate the stone. With the evaporation of the atmospheric water, the SO_4^{2-} will recrystallize within the pores of the stone as gypsum again or as other hydrated sulfates, exerting pressure on the walls of the pores and eventually causing the development of cracks. These new cracks can facilitate the further ingress of water and solubilized salts, and may account for the high sulfate content within the stone.[1]

In the spring of 1993, the author analyzed thin sections of stone samples from the column

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[1] The column at Mission San José exhibits the microcracking, scaling, and flaking typical of salt weathering, lending further credence to this theory concerning the source of gypsum in the stone. As well, the column appears to be the only architectural element in the convento on which gypsum was used as a bedding and patching mortar, and is the only element which displays massive deterioration due to salt contamination. The weathering and deterioration patterns of the column will be discussed further in Chapter 3.4 and Appendix C.

for mineralogical content and petrographical characterization.[2] The thin sections were observed and photographed under reflected and transmitted light using a polarizing light microscope at magnifications of 50X,100X, and 500X. The samples can be described as either impure, sandy limestone or calcareous sandstone, and were composed largely of angular grains of quartz sand in a cryptocrystalline calcite matrix (Figure 2.1). The angularity of the quartz indicates that the grains were not transported far from the parent rock. Traces of clays and feldspars were present, as were agglomerations of goethite which impart the golden-brown and reddish-purple coloring to the stone (Figure 2.2). Veins of calcite and possibly gypsum were observed in thin section; these minerals were deposited by water in hairline fractures after primary lithogenesis and prior to the quarrying of the stone (Figure 2.3). Numerous unfilled cracks were also visible, the products of post-quarrying deterioration mechanisms (Figure 2.2).

The water absorption rates of both badly weathered and relatively sound faces of the column were measured using Rilem PEM Test II.4, "Water Absorption Under Low Pressure (Pipe Method)." Sound surfaces of the column proved unexpectedly impermeable (Figure 2.4); the speed and massiveness of the column's deterioration had implied a stone of originally greater permeability and thus greater susceptibility to water penetration and its related deterioration mechanisms. Because the unsound surfaces were extremely friable, they were preconsolidated with 4 - 7.5 % v/v solutions of Acryloid B72 in 1:1 mixtures of toluene and xylenes prior to the water absorption test. B72 can significantly decrease water absorption rates (Chapter 1.5), but despite this, the deteriorated surfaces absorbed much more water than the sound surfaces (Figure 2.4).

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[2] I would like to thank Dr. Mary Emma Wagner of the Department of Geology at the University of Pennsylvania for her help in identifying the mineralogical composition of the stone.

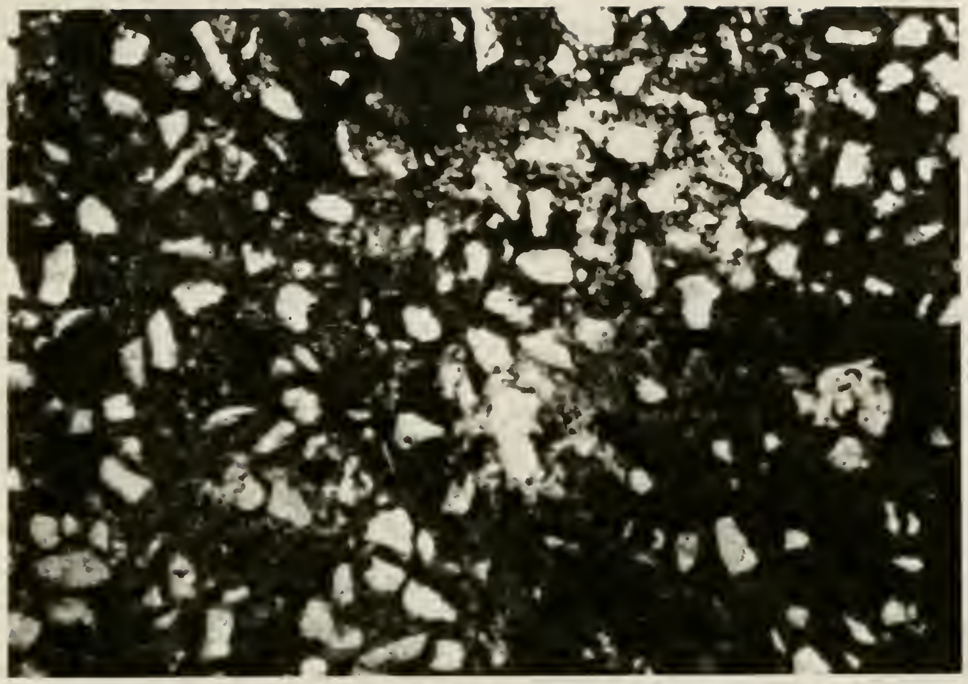

Figure 2.1 Thin section of convento column stone showing mineralogical composition under plane polarized light. Angular, transparent grains of quartz sand are embedded in the translucent, cryptocrystalline calcite matrix. Opaque areas are caused by the presence of goethite. Magnification 100X.

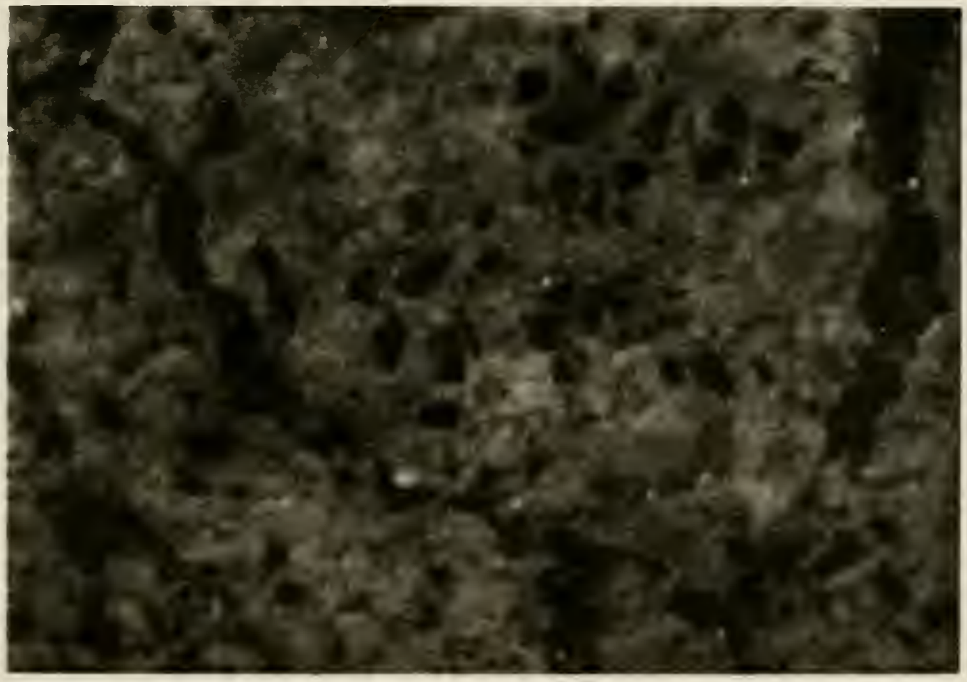

Figure 2.2 Thin section of convento column stone showing mineralogical composition and microcracking under reflected light. Angulr, non-reflective grains of quartz sand are embedded in a cryptocrystalline calcite matrix, made orange-yellow by the presence of goethite. Magnification 50X.

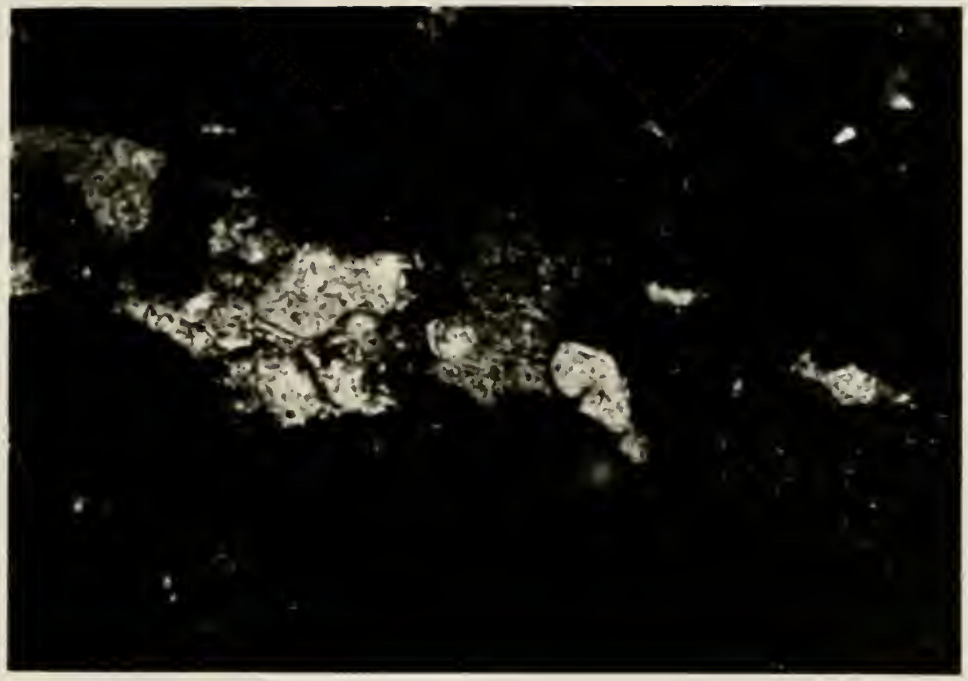

Figure 2.3 Thin section of convento column stone showing calcite replacement vein under crossed polars. Magnification 100X.

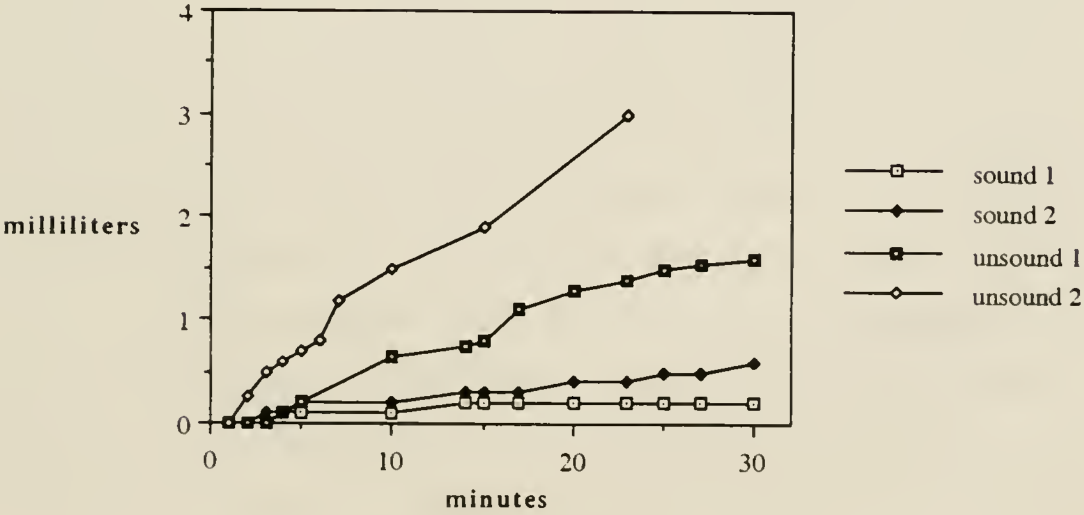

Figure 2.4 Water absorption rates of sound and unsound stone surfaces of the convento column, Mission San José y San Miguel de Aguayo, Texas.

These results illustrate the devastating effects of the cycling of calcium sulfate within the stone.

The results of the water absorption tests were used to estimate the permeability of the different stone surfaces. This information was useful in establishing a gradient of permeability from sound to unsound surfaces; the increase in permeability provided a measure of the extent of deterioration undergone by a surface. As well, because the effectiveness of consolidating materials is partly a function of their depth of penetration, the results of the water absorption tests were used to evaluate the potential effectiveness of these materials and to approximate the quantity necessary for treatment.

2.3 Selection of treatments

The determination of the types of treatment necessary to conserve the convento column stone were based upon the results of the characterization of the stone and its deterioration mechanisms, on the results of the conditions survey of the convento column (Appendix C), and on information derived from the literature review (Chapter 1). The stone, an impure limestone with a high content of quartz sand and lesser amounts of clay minerals, displayed localized deterioration associated with gypsum bedding mortar and patches, such that sound surfaces were interspersed with deteriorated surfaces. Sound surfaces did not require any consolidative treatments, but would benefit from the application of a water repellent. In contrast, the deteriorated areas displayed a combination of a loss of intergranular cohesion and larger-scale micro-cracking due largely to salt cycling, which resulted in excessive friability and flaking to a depth of up to 5 cm. These two types of deterioration required two types of treatment: first, a deeply-penetrating consolidant to re-establish intergranular cohesion; second, an adhesive to restore cohesion between larger

grains and to bridge gaps between flakes caused by microcracking. Water was the catalyst for deterioration: because the column is an exterior, load-bearing, architectural element, water cannot easily be removed from the system. Thus a third treatment was required: the application of a protective, water-repellent coating.

Three products were chosen to carry out the types of treatment listed above. Their selection was first based upon the degree to which they reflected the characteristics of an ideal consolidant and/or water repellent treatment (Chapter 1.3). Also the selection of these products was a function of their availability and their history of use and effectiveness as described in the conservation literature (Chapter 1), especially with respect to stones of similar composition manifesting similar deterioration patterns to those of the convento column.

Acryloid B72 was chosen as the adhesive, and is a 50/50 copolymer of methyl methacrylate and ethyl acrylate (Wheeler et al., 1991). Dow Corning Silane Z6070 was chosen as the water repellent, and is composed of 97% by weight methyl trimethoxysilane, 1% dimethyl dimethoxysilane, and 2% methanol.[3] For clarity, these products will hereafter be referred MMA (methyl methacrylate) and MTMOS (methyl trimethoxysilane). MMA and MTMOS have been used as consolidants for stone, both separately and in mixtures (Chapter 1). However, because the deterioration of some sections of the column was quite deep and the depths of penetration of MMA and MTMOS are limited, a more deeply-penetrating material was deemed necessary. Thus Conservare Stone Strengthener OH was chosen as the consolidant; it is an ethyl silicate

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[3] Acryloid B72 is manufactured by Rohm and Haas, with headquarters at Independence Mall West, Philadelphia, PA, 19107, (215) 592-3000, but is available only through distributors. Dow Corning Z6070 Silane is manufactured by Dow Corning Corporation, South Saginaw Road, Midland, MI, 48686, (517) 496-6000, and is also only available through distributors.

composed of 75% by weight silicic ethyl esters in a solvent of methyl ethyl ketone, and possesses excellent depth of penetration; it will hereafter be referred to as OH.[4]

After the selection of the initial consolidant, a decision had to be made concerning the manner in which the adhesive and water repellent would be applied. Mixtures have proven to be effective and are widely used for the consolidation and protection of stone. The use of a mixture would seem most logical, but two considerations spoke against its use:

- The deterioration of the column was quite localized, and in sound areas it was not appropriate to introduce the adverse effects of color change and reduction of water vapor permeability known to be caused by acrylics. However, the sound areas would benefit from a protective, water-repellent coating.

- After consolidation, large areas of loss were designated to be infilled with a lime-based patching material to restore the visual coherence and the structural integrity of the column. While it was necessary to stabilize the friable surfaces with both a consolidant and an adhesive prior to infilling, a hydrophobic surface would interfere with the adherence of these patching materials.

Thus it was proposed to apply the consolidant (OH) to the entire column, apply the adhesive (MMA) to all friable areas, apply the patching material in designated areas, and finally apply the water repellent (MTMOS) to the entire column. This sequential

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[4] Conservare Stone Strengthener OH is manufactured and sold by ProSoCo, Inc., PO Box 1578, Kansas City KS, 66117, (913) 281-2700.

application of the consolidant, adhesive, and water repellent was considered more practical, flexible, and potentially more effective than a mixed treatment. However, few records of this type of sequential treatment were found in the literature, and it was not known if a sequential treatment would render the same effectiveness as a mixed treatment, or how the application of the water repellent over the adhesive would affect the physical, mechanical, or chemical properties of either substance (see Chapter 1 for a detailed discussion). The informed and appropriate selection of one of these two treatment methods was paramount, so an experimental program was devised to measure specific differences in the physical and mechanical properties of the stone resulting from the different treatment methods.

2.4 Accelerated weathering of stone samples

San Antonio Missions National Historical Park provided two-inch, saw-cut cubes of stone from the perimeter walls of Mission San José, similar in color and texture to that of the column, for pretreatment testing. This stone was weathered but not highly deteriorated, and had the low permeability typical of the sound surfaces of the column stone. Thus, prior to treatment, a program of accelerated weathering was necessary to ensure that the conservation materials would be absorbed and that the relative effects of the two application methods would be measurable. The choice of standardized laboratory methods for weathering the samples was based upon the results of the characterization of the convento column stone and its deterioration mechanisms. The methods were applied to the samples to approximate the weathering mechanisms acting on the column and to achieve the resultant deterioration patterns displayed by the column stone.

Salt cycling was chosen as the primary accelerated-weathering method because it would

simulate both the cause of deterioration and the effects, namely the scaling, flaking, and cracking exhibited on the column. Methods were based upon ASTM C 88-90, "Standard Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate," which was designed to measure the soundness of aggregates used in concrete when subjected to salt weathering. These methods were modified using RILEM 25 P.E.M. Test V.1a, "Crystallisation Test by Total Immersion (for Untreated Stone)." Forty-four samples were immersed in a saturated sodium sulfate solution kept at 20 ± 1°C for 4 hours, followed by drying in an oven at 115 ± 5°C for 16-17 hours. The samples were then removed from the oven and allowed to cool for 3-4 hours; this process constituted one cycle. After thirteen cycles, four samples showed significant weight loss and deterioration patterns similar to those of the convento column stone; however, the other forty samples showed little to no change in weight or appearance.

Because of the minimal deterioration achieved using salt cycling alone, the samples were immersed in a bath of 1M sulfuric acid (H_2SO_4) for 18 hours in an attempt to dissolve some of the calcium carbonate binder, increase the permeability of the stone, and thus allow for increased penetration of salts when salt cycling was resumed. After removal from the acid bath, the samples showed an average weight loss of 0.7% and their surfaces were quite friable. After thorough rinsing the samples were subjected to five salt cycles, which again had little effect on their weight or appearance.

Because of the failure of sulfuric acid to increase the permeability of the stone, the samples were immersed in a bath of 1M hydrochloric acid (HCl), which had a visibly more destructive effect on the calcium carbonate binder. Following this second acid bath, one sample was stained with a 0.5M solution of copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$]. Copper nitrate stains calcite a turquoise blue and stains non-carbonate minerals a paler

blue; it was used in this instance to estimate the extent of calcium carbonate loss due to acid weathering and also to determine the depth of penetration of the stain, thus revealing the permeability of the stone (Dolar-Mantuani, 1983). After immersion in the copper nitrate solution for 18 hours, the sample was removed, dried, and broken open with a hammer. Staining revealed that the acid baths had eliminated the calcium to a depth of less than 0.5 mm; the failure of the stain to penetrate any deeper than 0.5 mm indicated that the effects of the acid were entirely superficial, and that no real increase in permeability had been achieved.

2.5 Formulation of facsimiles

Because of the impermeability of the stone samples, it was not possible to weather them sufficiently in the given time (two months) to allow for the administration of the treatments and the evaluation of the effects of the different application methods. Instead, "facsimiles" were formulated and manufactured to provide a basis for the comparative evaluation of the two methods. The facsimiles were in no way intended to replicate the chemical or physical properties of the limestone, and the quantitative results of the experimental program cannot be inferred to correlate to the column stone. But certain advantages are derived from treating and testing the facsimiles rather than the stone samples. Because the same treatments were applied to all of the facsimiles, the method of their application was the only variable. Thus the primary purpose of the experimental program was not to measure the effectiveness of the individual treatments in consolidating the substrate but to measure the effects of the treatments on each other, which thereby influenced their effectiveness in consolidating the substrate. Because the facsimiles were more uniform in composition than the stone samples, variations in the test results of different treatment groups could be assumed to be caused by the interaction of the

treatments with each other rather than by inconsistencies in the substrate; the uniformity of the facsimiles also allowed for more statistically comparable test results. Because the facsimiles were inherently weak, measurable test results could be obtained, which was not possible with the impermeable, unweathered stone samples. Thus, although the quantitative results of the experimental program cannot be applied to the column, qualitative comparisons of the relative effectiveness of the two methods of application, as a result of their interaction, can be made. The information derived from these comparisons is valid not only for the specific instance of the limestone column but for the general conservation of stone.

The facsimiles consisted of equal parts sand and marble dust, a chemically stable form of calcium carbonate.[5] Water was added until the mixture was of a plastic consistency, or about 15% by weight of the dry ingredients. Because the calcium carbonate was chemically stable, cohesion of the facsimiles relied solely on mechanical bonds, rendering them quite weak and susceptible to weathering, and ultimately allowing for measurable differences between types of application methods. In essence, the facsimiles represented a worst-case scenario of the column stone, in which all intergranular cohesion had been lost.

Marble dust, sand, and water were mixed in accordance with ASTM C 305-82 (reapproved 1987), "Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency," and packed into steel cube molds 2" square or plastic disk molds 2 3/4" in diameter and 3/4" high. These had been sprayed with a

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[5] The sand used was Morie Filter Sand #0, sold by The Morie Co., Inc., 1201 N. High St., Millville, NJ, 08332. The sand, light brown in color, was sieved for grain size characterization using ASTM sieves, with the following percents passing: #8 : 100%; #16 : 99.9%; #30 : 83.7%; #50 : 20.9%; #100 : 1.1%; #200 : 0.0%.

greaseless lubricant to facilitate the removal of the facsimiles from the molds.[6] Facsimiles were allowed to set in the molds for 12-24 hours; upon removal, they were placed in a 60 ± 5°C oven to dry for 48 hours. A total of 40 cubes and 16 disks were manufactured for testing purposes.

The finished facsimiles did cohere, but were powdery and friable to the touch. Because of this inherent weakness, it was not necessary to preweather the facsimiles to obtain measurable results from conservation treatments.

2.6 Treatment of facsimiles

Four categories of facsimiles were created by applying the three products listed above and were designated by two-letter codes as follows:

1. CT : no treatment, acting as control
2. OH : treatment with OH only
3. SQ : treatment with OH followed by sequential applications of MMA and MTMOS
4. MX : treatment with OH followed by an application of a mixture of MMA and MTMOS

Treatments were administered by both partial immersion and brush application. All of the disks and most of the cubes were treated by partial immersion; the treatments rose

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[6] LPS Greaseless Lubricant, composed of an aliphatic hydrocarbon and petroleum naptha, and manufactured by LPS Laboratories, Inc., Tucker, GA, 30085-5052 (800) 241-8334.

through the samples by capillarity until complete saturation was obtained, reducing the possibility of air entrapment which might have occurred if the samples had been completely immersed. Treatments were brush-applied to the twelve samples designated for the depth of penetration test. The following are detailed descriptions of treatments separated by facsimile category and method of treatment application:

CT: The untreated control facsimiles were placed on racks after oven drying, and were not disturbed until the advent of the testing program.

OH (partial immersion): The facsimiles were placed on glass beads in a solvent-resistant plastic container and partially immersed in undiluted OH to a depth of 1/3 of the sample height. The container was then sealed to prevent the evaporation of the solvent. The OH rose by capillarity, producing a darkening of the facsimiles where saturation had occurred. When all surfaces were saturated (after about 2 hours at about 20°C), the facsimiles were rotated 180° on a horizontal axis and allowed to soak for 30 minutes. The facsimiles were then removed from the bath and placed on metal racks to cure for fifteen days. The racks were loosely draped in plastic sheeting to prevent the rapid evaporation of the solvent while allowing for sufficient air circulation.

OH (brush application): A soft-bristled, synthetic-fiber brush was dipped in undiluted OH. The brush was lightly wiped against the sides of the container to remove excess material, and was then brushed twice over the top surface of a single facsimile. This process was repeated three times at 5 minute intervals for each facsimile in accordance with the manufacturer's instructions. The facsimiles were then placed on the drying racks for fifteen days.

SQ (partial immersion): The facsimiles were first treated with OH in the above manner. After curing, the facsimiles were partially immersed in like manner in a 5% w/v solution of MMA in toluene. The MMA rose more slowly than the OH, stopping at about 2/3 the height of the cubes after 2 hours. The cubes were then rotated 90° on a horizontal axis and again partially immersed for 2 hours; finally the cubes were rotated 180° on a horizontal axis and partially immersed in MMA for 16 hours. Following the initial 2-hour immersion, the disks were rotated 180° and immersed for 2 hours, after which time they appeared saturated and were removed from the solution. All facsimiles were placed on covered metal racks as described above and left to dry for four days.

After drying, the cubes and disks were partially immersed in a 100% solution of MTMOS. Immersion times and procedures were the same as those used for the application of MMA described above. Facsimiles were then placed on the drying racks for seven days.

SQ (brush application): Cubes (previously treated with brush-applied OH) were brushed with a 5% w/v solution of MMA in toluene using the same method described for the brush application of OH. The facsimiles were placed on the drying racks for 4 days. Lastly a 100% solution of MTMOS was brush-applied in the same fashion, and the facsimiles were placed on the drying racks for seven days.

MX (partial immersion): Facsimiles previously treated with OH were partially immersed in a 5% w/v solution of MMA dissolved in undiluted MTMOS. Immersion times and procedures for cubes and disks were the same as those used

for the application of MMA described above. The facsimiles were then placed on the drying racks for fourteen days.

MX (brush application): Cubes previously treated with brush-applied OH were brushed with a 5% w/v solution of MMA in undiluted MTMOS using the same method described for the brush application of OH. The facsimiles were placed on the drying racks for fourteen days.

After complete curing and drying, the facsimiles were labelled with a four-character code to designate the type of treatment they had received and the test for which they were designated. A complete list of facsimiles and codes is provided in Table 2.1. The first letter refers to the test for which the facsimile was designated; the number is the facsimile number within that test; the following two letters refer to the treatment applied to the facsimile; e.g., S10.SQ refers to the tenth facsimile designated for the salt crystallization test, which was treated with OH plus a sequence of MMA and MTMOS.

2.7 Experimental program

An experimental program was designed to evaluate the sequential and mixed treatment methods described above. Tests were selected to measure several important properties of stone consolidating materials as outlined in Chapter 1.3. On a practical level, selection was also a function of time and the limited accessibility of instrumentation. The selected tests can be divided into two categories: those which quantify the differences in the properties of the products (e.g., depth of penetration, microstructure, % retention) as a result of the method of their application (sequence or mixture), and those which quantify changes in the properties of the substrate as a result of these different application methods

Table 2.1 Schema for the labeling of facsimiles

DESIGNATED TESTING
N = non-destructive tests
D = depth of penetration test
S = salt crystallization test
V = water vapor transmission test

DESIGNATED TREATMENT
CT = untreated control
OH = OH only
SQ = OH + MMA + MTMOS
MX = OH + MMA in MTMOS

--	--	--	V1.CT
--	--	--	V2.CT
--	--	--	V3.CT
--	--	--	V4.CT
N5.OH	D5.OH	S5.OH	V5.OH
N6.OH	D6.OH	S6.OH	V6.OH
N7.OH	D7.OH	S7.OH	V7.OH
N8.OH	D8.OH	S8.OH	V8.OH
N9.SQ	D9.SQ	S9.SQ	V9.SQ
N10.SQ	D10.SQ	S10.SQ	V10.SQ
N11.SQ	D11.SQ	S11.SQ	V11.SQ
N12.SQ	D12.SQ	S12.SQ	V12.SQ
N13.MX	D13.MX	S13.MX	V13.MX
N14.MX	D14.MX	S14.MX	V14.MX
N15.MX	D15.MX	S15.MX	V15.MX
N16.MX	D16.MX	S16.MX	V16.MX

(e.g., color change, permeability, water vapor transmission, resistance to salt crystallization).

To comply with testing standards and to ensure statistical precision and significance, four facsimiles of each category, namely CT, OH, SQ, and MX, were used whenever possible, totalling sixteen samples per test. However, because the CT facsimiles were water-soluble, untreated controls could not be used for tests involving immersion in water, including salt crystallization, absorption, and bulk specific gravity. In their place,

facsimiles treated with OH only were used as controls, thus totalling twelve samples per test.

2.7.1 Depth of penetration

Standardized tests used

None. The following test is based upon a procedure recommended by Weber and Zinsmeister (1991) and modified by the author.

Purpose

To measure the depths of penetration of three separate brush-applied treatments: OH, SQ, and MX, and to determine whether statistically significant differences exist between the depths of penetration of the three treatments.

Significance

To be effective and to prevent the formation of a surface crust, a conservation treatment must penetrate through the deteriorated or altered zone and into the sound core of the stone. A comparison of the depths of penetration of the SQ and MX treatment methods allows a measurement of the different effects, if any, of applying MMA and MTMOS in sequence and in mixture, which in turn provides a better basis for the recommendation of a treatment.

Methodology

Brush-applied treatments administered to a total of twelve facsimiles were examined for their depth of penetration; four cubes each had been treated with OH, SQ, and MX. Samples were broken in half with a hammer and chisel perpendicular to the treated face, wetted with deionized water, and dabbed of excess moisture with a damp cloth. Untreated surfaces darkened and appeared wet, while treated surfaces did not discolor and appeared dry and granular (Figures 2.5a and 2.5b). The wetted samples were then

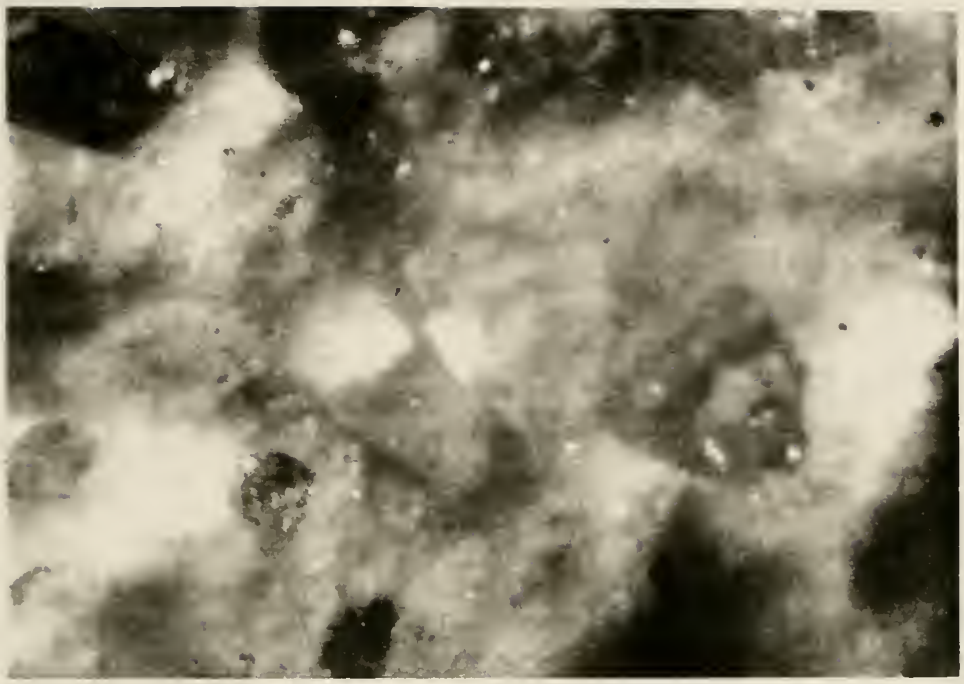

Figure 2.5a Cross-section of wetted sample D14.MX, showing discoloration and moisture retention where treatments did not penetrate (reflected light, 50X magnification).

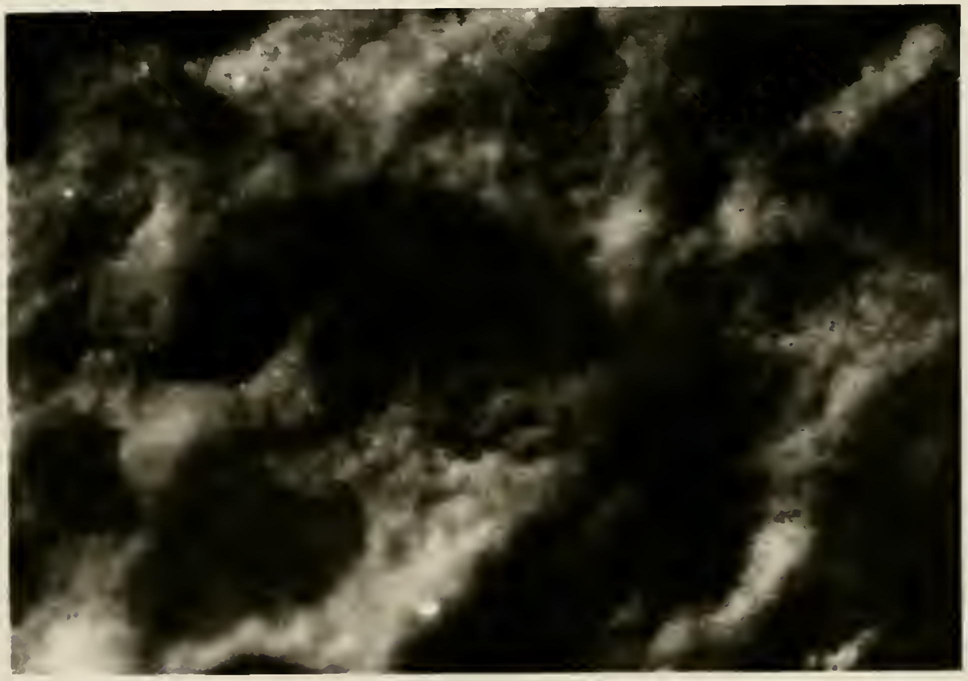

Figure 2.5b Cross-section of wetted sample D14.MX, showing granularity and driness where treatments penetrated (reflected light, 50X magnification).

placed under a microscope at 50X magnification in reflected light; using an eyepiece reticle, measurements of the width of the treated surface (equivalent to the depth of penetration) were taken at three or more locations on each sample.

Depth of penetration measurements were recorded in units of the eyepiece reticle, where 1 unit = 0.025 mm (Appendix B, Table B.1). To prevent a false degree of precision in the results, the reticle units were not converted to millimeters until after all calculations were completed.

Results

The depths of penetration of the treatments were measured for each facsimile, and then the mean value and standard deviation were calculated within each treatment group. From the mean values, the % increases in the depths of penetration of the treatments in relation to the OH treatment group were also calculated (Table 2.2).

Table 2.2 Mean depth of penetration and % increase in depth of penetration with respect to the OH facsimiles

	OH	SQ	MX
mean (mm)	2.43	2.53	2.88
standard deviation	±15.4	±15.1	±13.1
% increase	0.0	4.0	16.0

The F-test and the t-test were used to statistically analyze the test results. Using the F-test, the standard deviations of the three treatment groups were compared to determine if there was any significant difference in the precisions of the results of each test group; no

significant differences existed between the precisions of any of the treatment groups. Using the t-test, the means of the three groups were compared to determine if there were significant differences in the depth of penetration of the different treatments. The levels of probability of significant differences between the means of the treatment groups are reported in Table 2.3.

Table 2.3 Significant differences in the mean depths of penetration of statistically comparable treatment groups

treatment group	hypothesis test result
OH - SQ	not significant
OH - MX	significant at the 1% level of probability
SQ - MX	significant at the 5% level of probability

Discussion and conclusions

Based upon a comparison of the means, the conservation treatment method involving the application of OH followed by the application of a mixture of MMA and MTMOS achieved the deepest penetration in the facsimiles. As well, the differences between the depths of penetration of OH and MX and between SQ and MX proved to be statistically significant, while no significant difference existed between OH and SQ. Based upon these results, a mixture of MMA and MTMOS could be recommended over the sequential application of the same products; it is worthy of note, however, that the mean depths of penetration of all three treatments were much less than the depth of approximately 25 - 50 mm recommended in the conservation literature. In part, these low depths of penetration may be a result of the very uniform and small grain size of the marble dust in the facsimiles, which would result in a low porosity and permeability.

As previously stressed, the facsimiles do not replicate the permeability or geochemical composition of the limestone of the convento column. The actual depth of penetration of the treatments in the limestone cannot be derived from the above figures. Ideally, test patches of the prospective treatments would be applied to the column and then drill cores taken to measure the depth of penetration; the small size and the visibility of the column precluded this option. However, based on the statistical analysis one can presume that the application of a mixture of MMA and MTMOS, as opposed to the sequential application of the same substances, may increase the depth of penetration of at least these two conservation materials.

Because the OH cured fully before the application of either the sequence or the mixture, the solvents (toluene and methanol) used as the carriers for MMA and MTMOS should have had no effect on the OH (e.g., resolubilizing and thus redistributing the ethyl silicate). Thus the increased depth in penetration of the mixture is the result of the increased penetration of MMA dissolved in MTMOS. Although outside the scope of this study, it would be helpful to measure the depth of penetration of MMA and MTMOS separately, in sequence, and in mixture without the addition of OH in order that the depths of penetration of the individual substances and their effects on one another might be understood more fully.

Past studies indicate that the addition of MMA to MTMOS increases the depth of penetration of the latter, which at first seems contradictory. The viscosity of MTMOS is very low, allowing for potentially excellent depth of penetration, but its volatility is high and much evaporative loss can occur in the initial stages of polymerization. Logically, the addition of the large acrylic molecule would decrease the depth of penetration of the MTMOS, but it does not. This may be because the MMA "entraps" the MTMOS within

the acrylic polymer network, thus preventing evaporative loss of the highly-volatile silane and promoting its condensation in the stone. By this means, the initially good depth of penetration of MTMOS, although somewhat reduced by the addition of MMA, is maintained to some degree (Chapter 1.6.1 and 1.6.4). The above test results seem to support this observation, and also indicate that, in a sequential application, the polymerized MMA does not "entrap" the MTMOS or cause a similar increase in depth of penetration.

2.7.2 Microstructure

Standardized tests used

None. Etching of samples for SEM by using 1M HCl was based upon procedures used by Charola et al. (1984) and de Witte et al. (1985), and modified by the author.

Purpose

To establish visual references for one untreated facsimile and three facsimiles treated with OH, MMA, or MTMOS alone, and to observe if any differences in deposition and film morphology resulted from a mixed versus a sequential application of MMA and MTMOS when applied to facsimiles previously treated with OH.

Significance

Uneven deposition, reverse migration, or segregation of the MMA and MTMOS would provide potential sources of weakness and lead to the eventual failure of a treatment. Of greatest concern would be the deposition of the MMA consolidant only on the surface of the treated substrate. In this event, an artificially strong crust would overlay unconsolidated (thus weaker) interior material; as well, the segregated layer of MMA might also inhibit water vapor transmission, and the recrystallization of soluble salts would take place behind the surface crust in the weaker layer, eventually causing the surface crust to spall. Also the microstructure of the resultant polymer networks, particularly their continuity and the manner in which they bond with the substrate, affects the short- and long-term performance of the conservation treatments.

Methodology

Scanning electron microscopy was used to characterize the microstructure and appearance

of the untreated facsimiles and those treated with OH, MMA, or MTMOS only. Once these visual references had been established, samples which had been brush-applied with OH plus a sequence or a mixture of MMA and MTMOS were examined to compare the microstructures resulting from the two methods of application. (Neither MMA nor MTMOS, nor the method of their application, should have any effect on the inorganic SiO_2 matrix formed by the cured OH).

A total of six samples (CT, OH, MMA, MTMOS, SQ, and MX) were first etched with 1M HCl as recommended by Charola et al. (1984) for carbonate rocks, then dessicated, and finally sputter-coated with gold to a thickness of approximately 720 Angstroms. The six samples were then examined using scanning electron microscopy.[7] The zones immediately beneath the surfaces of all samples were examined and photomicrographs taken at magnifications ranging from 250X to 10,000X.

Results

Results are in the form of photomicrographs, which are reproduced in Figures 2.6 - 2.11c.

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[7] Samples were examined at the Laboratory for Research on the Structure of Matter, University of Pennsylvania, using a JEOL 6300FV scanning microscope. I would like to thank Xue Qin of the LRSM for her patience and help in preparing samples and using the equipment. This portion of the research was supported by the National Science Foundation MRL Program, under Grant No. DMR91-20668.

I would also like to thank Frank Matero for preparing and photographing the final batch of samples treated with a mixture of MMA and MTMOS, Figures 11a, 11b, and 11c.

Figure 2.6 SEM photomicrograph of untreated and unetched facsimile (CT). Larger grains are quartz sand and smaller grains are marble dust (calcium carbonate). 3.0KV, 1000X magnification.

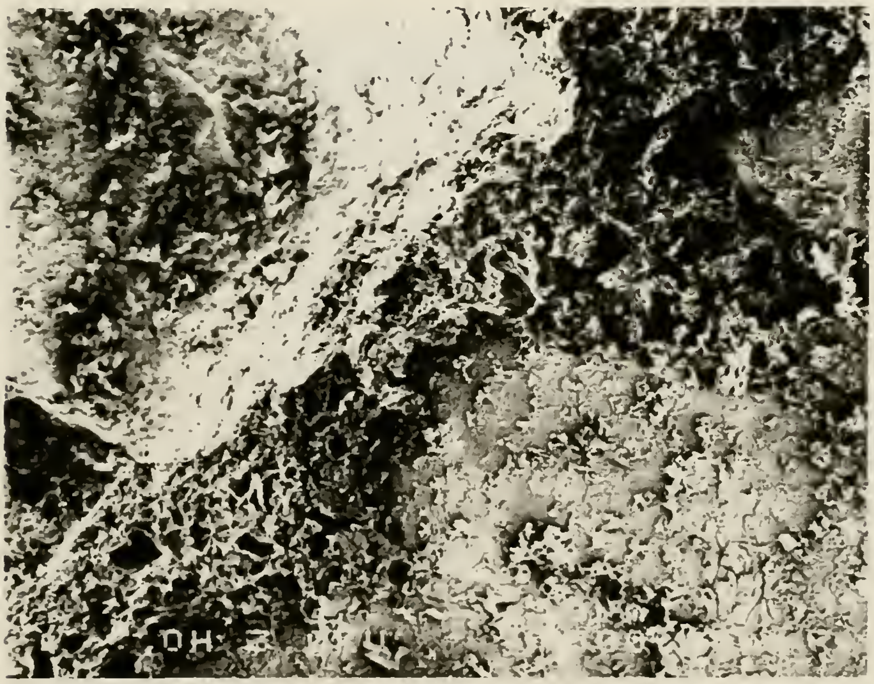

Figure 2.7 SEM photomicrograph of facsimile treated with ethyl silicate (OH) only and etched with 1M HCl. 3.0KV, 500X magnification.

Figure 2.8 SEM photomicrograph of facsimile treated with an ethyl methacrylate/methyl acrylate copolymer (MMA) only and etched with 1M HCl. 3.0KV, 500X magnification.

Figure 2.9 SEM photomicrograph of facsimile treated with methyl trimethoxysilane monomer (MTMOS) and etched with 1M HCl. 3.0KV, 500X magnification.

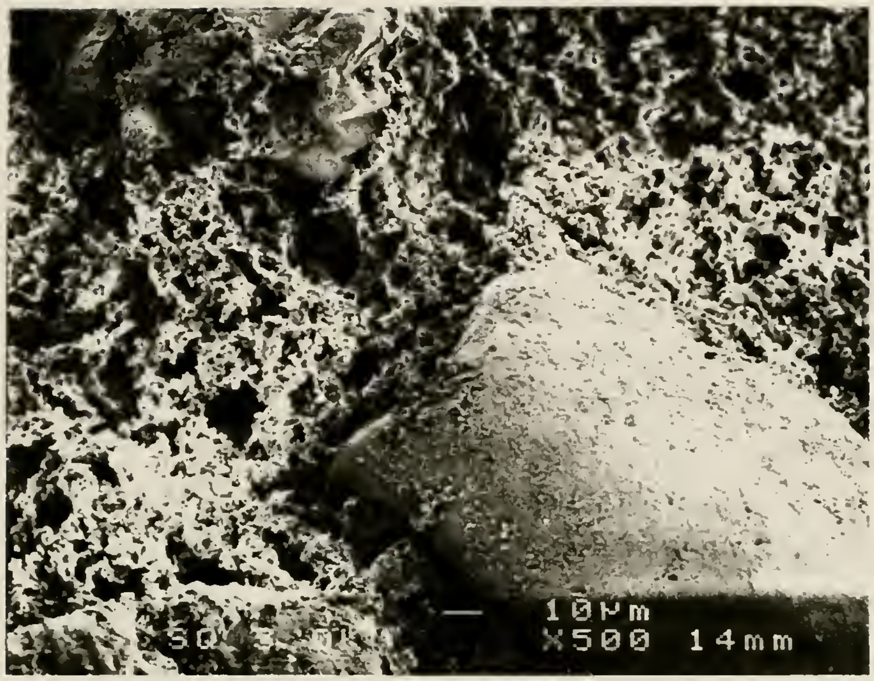

Figure 2.10a SEM photomicrograph of facsimile treated with OH followed by sequential applications of MMA and MTMOS (SQ) and etched with 1M HCl. 3.0KV, 500X magnification.

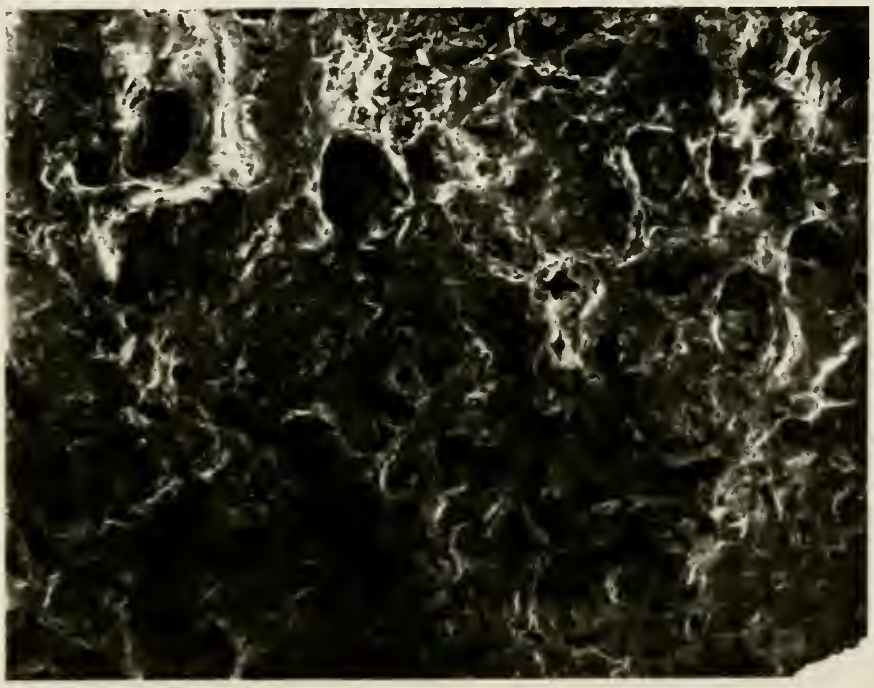

Figure 2.11a SEM photomicrograph of facsimile treated with OH followed by a mixture of MMA and MTMOS (MX) and etched with 1M HCl. 3.0KV, 500X magnification.

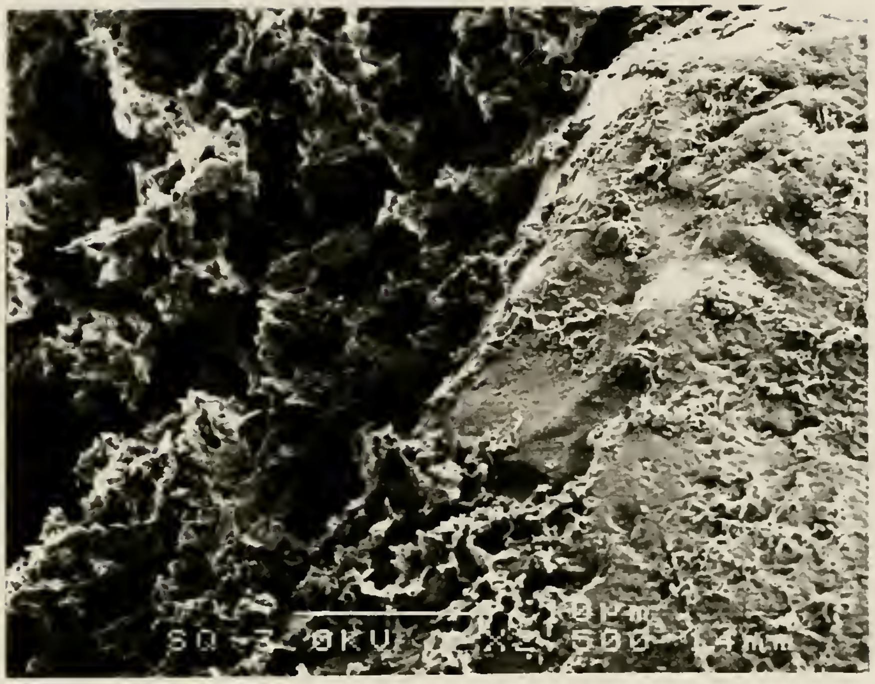

Figure 2.10b SEM photomicrograph of facsimile treated with OH followed by sequential applications of MMA and MTMOS (SQ) and etched with 1M HCl. 3.0KV, 2500X magnification.

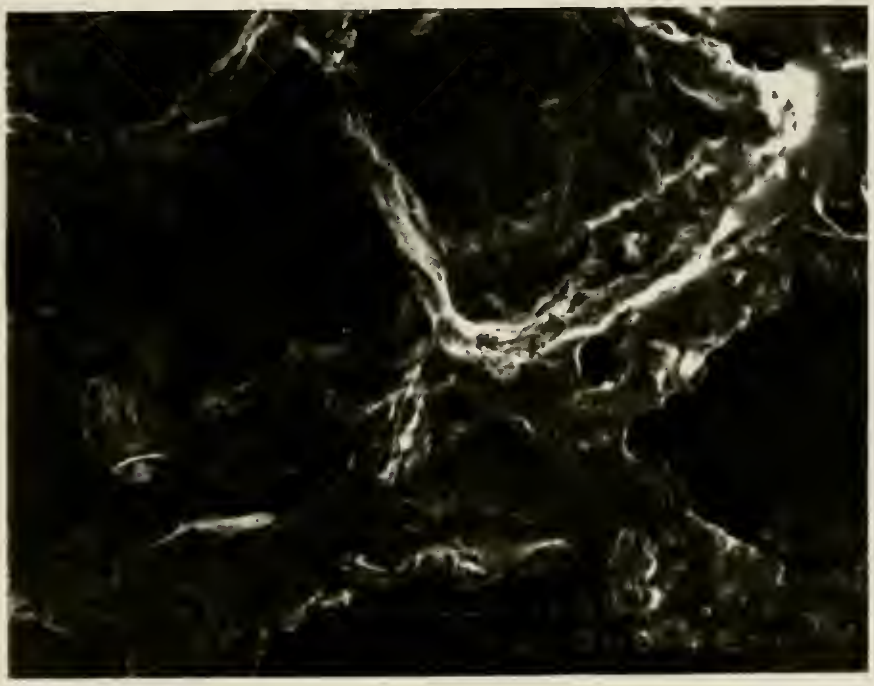

Figure 2.11b SEM photomicrograph of facsimile treated with OH followed by a mixture of MMA and MTMOS (MX) and etched with 1M HCl. 3.0KV, 2500X magnification.

Figure 2.10c SEM photomicrograph of facsimile treated with OH followed by sequential applications of MMA and MTMOS (SQ) and etched with 1M HCl. 3.0KV, 10000X magnification.

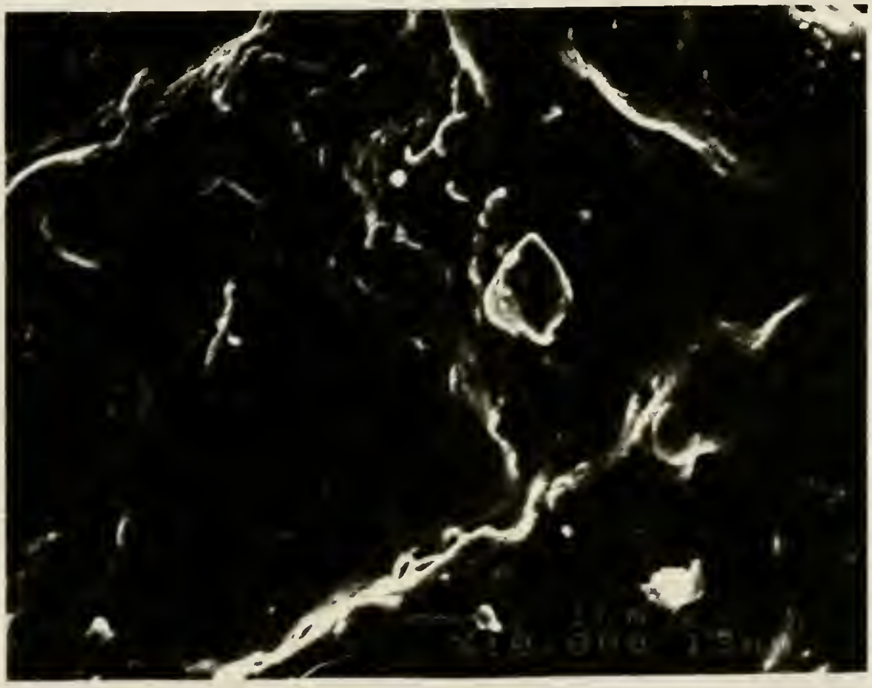

Figure 2.11c SEM photomicrograph of facsimile treated with OH followed by a mixture of MMA and MTMOS (MX) and etched with 1M HCl. 3.0KV, 10000X magnification.

Discussion and conclusions

The SEM photomicrographs of each treatment are discussed in detail below:

- **CT** (control): the microstructure of the untreated and unetched facsimiles is visible in Figure 2.6. The large grain on the left side of the image is quartz sand, which is surrounded by a matrix of flat calcite crystals and smaller cryptocrystalline calcite particles which have a more powdery appearance.

- **OH** (ethyl silicate): the microstructure of OH is visible in Figure 2.7. OH forms a discontinuous but uniformly deposited film, which is apparently glassy and brittle, over the surface of the two large quartz grains visible in the photomicrograph. Some of the voids in the OH film are the "ghosts" of calcite grains before they were dissolved in the etching process.

- **MMA** (ethyl methacrylate/methyl methacrylate copolymer): the microstructure of MMA is visible in Figure 2.8. The film is discontinuous and uneven in deposition, but MMA appears ropy and more flexible than OH and is able to bridge large voids between quartz grains. This accounts for the excellent adhesive properties of MMA. Again, some voids indicate the location of calcite grains before etching, but several etched calcite crystals are visible on the left side of the image. These are held in place by the polymer formed MMA, and their presence even after prolonged immersion in HCl may be a result of the hydrophobic properties of newly-cured MMA.

- **MTMOS** (methyl trimethoxysilane monomer): the microstructure of MTMOS is visible in Figure 2.9. In appearance, MTMOS falls somewhere between that of

OH and MMA, appearing more flat and brittle than MMA but more flexible and capable of bridging larger voids than OH. MTMOS forms a thin but relatively even and continuous film over the large quartz grain visible in the image. Many small calcite grains are visible even after prolonged etching, the result of the hydrophobic properties of MTMOS.

- **SQ** (OH + MMA + MTMOS): The microstructure of SQ is visible in Figures 2.10 a, 2.10b, and 2.10c. In appearance, SQ is almost identical to OH, forming a glassy and discontinuous film. The presence of MMA and MTMOS is difficult to discern. At higher magnifications SQ appears less flat and more flexible than OH. Again, voids indicate the location of calcite grains prior to etching; few calcite particles are visible after etching.

- **MX** (OH + MMA/MTMOS): The microstructure of MX is visible in Figures 2.11a, 2.11b, anbd 2.11c. In appearance, MX forms a thin and continuous film; the brittle and discontinuous OH pretreatment is no longer visible and is presumably overlaid by the MX treatment. The smoothness and continuiuty of the film indicate the uniform dissolution of MMA in MTMOS, as does the somewhat ropy nature of the film, visible as ridges around voids. Although these voids indicate that calcite grains were lost from the surface during etching, many others are still held within the MX matrix and are also visible in the layer immediately beneath the film. This physical "locking-in" of calcite grains, for which MTMOS and MMA have no chemical affinity, was also observed by Charola et al. (1984b).

Based upon the observed quantity of material deposited on the facsimiles, treatments with

mixtures of MMA and MTMOS could be considered more effective than treatments with sequences of the same. The inhomogeneity of the SQ film and the contrasting homogeneity of the MX film is also a function of quantity rather than of any visible segregation or irregular deposition of the two materials. Wheeler et al. (1991) found that when MMA and MTMOS were applied in a mixture, the MMA "entrapped" the MTMOS material, preventing its evaporative loss and promoting condensation at later stages of polymerization. From the above images, it would appear that cured MMA does not entrap the MTMOS material.

One major difference in the application of MMA and MTMOS in sequence versus mixture is that toluene is used to dissolve the MMA in the sequential application, while the methanol intrinsic to the MTMOS is used to dissolve the MMA in the mixed application. The vapor pressure of methanol (95 mmHg at 20°C) is higher than that of toluene (22 mmHg at 20°C). Although MMA entraps MTMOS at later stages of polymerization, the presence of MMA in the MTMOS solution has no effect on initial evaporative loss (Wheeler et al., 1991). Methanol, the more volatile solvent, may reduce the dwell time and induce the reverse migration of the MMA/MTMOS mixture at initial stages of polymerization, resulting an accumulation of MX at the surface of the treated object, the presence of which we may be observing in Figures 2.11a - 2.11c. In contrast, the lower volatility of toluene should allow for the deeper penetration of MMA in the first stage of the sequential application. However, cured MMA remains reversible in organic solvents. When MTMOS is applied to a surface previously treated with MMA, the MMA may be redissolved in the methanol solvent used to dissolve the MTMOS. This would induce the reverse migration and loss of both MMA and MTMOS as the methanol evaporates.

The latter hypothesis is supported by the results of the bulk specific gravity test (Chapter

2.7.5), which indicates that considerably less MMA and MTMOS are deposited on SQ facsimiles than on MX facsimiles. However, the results of other tests, including the improved resistance of facsimiles treated with SQ to water absorption (Chapter 2.7.4) and to salt crystallization (Chapter 2.7.7), indicate that more MMA and MTMOS are deposited on the facsimiles than is visible in the SQ photomicrographs. Most importantly, only one SQ sample was examined, and the average appearance of SQ treatments cannot be generalized from these images. No other SEM examinations of the effects of sequential applications of MMA and MTMOS on microstructure were found in the literature. However, SEM examination of the microstructure of MMA/MTMOS mixtures has been conducted, and the appearance of the above MX photomicrographs is consistent with those images (Tucci et al., 1985; Charola et al., 1984; Charola et al., 1982).

In future attempts to characterize the microstructures of SQ and MX treatments, it would be helpful to examine a greater number of samples per treatment group in order that accurate generalizations might be made. Also, only the layer immediately beneath the surface was examined using SEM, and the morphologies of the films further beneath the surface and immediately at the surface should also be studied. Most importantly, by examining sequence samples at each stage of treatment, i.e., after OH, after MMA, and after MTMOS treatments, rather than at the conclusion, the effects of later treatments on the microstructure and distribution of the previous ones might be more fully understood.

2.7.3 Color change

Standardized tests used

ASTM D 1535 - 80, "Standard Method of Specifying Color by the Munsell System," matte book

Purpose

To determine the effects, if any, of the OH, SQ, and MX conservation treatments on the color of the facsimiles.

Significance

The ideal conservation treatment should have no short- or long-term effect on the optical properties of the treated stone, including hue, value, chroma, and reflectance (gloss). Any change in these properties is undesirable, and the treatment with the least effect on the optical properties of the stone should receive primary consideration. Measuring any changes in color or reflectance (both immediately after treatment and after weathering) caused by the different conservation treatments allows for a more informed selection of the best treatment for the stone.

Methodology

The color change caused by the different treatments was measured by a visual reference standard using Munsell matte colors. A total of one untreated control and five facsimiles, each brushed with a different type of treatment, were measured: untreated control (CT), treated with OH only (OH), treated with MMA only (MMA), treated with MTMOS only (MTMOS), treated with OH followed by MMA followed by MTMOS (SQ), and treated with OH followed by a mixture of MMA dissolved in MTMOS (MX).

Results

The results of the color change test are reported in Table 2.4.

Table 2.4 Color changes in facsimiles caused by conservation treatments

treatment group	hue value/chroma
CT	N 9.25/
OH	N 9.25/
MMA	N 9.5/
MTMOS	N 9.25/
SQ	N 9.5/ - 5Y 8.5/1 = 2.5Y 9/.5
MX	N 9.5/ - 5Y 8.5/1 = 2.5Y 9/.5

Discussion and conclusions

The Munsell matte color N 9.25/ was determined (by the author) as the original color of the facsimiles. As shown by the results (Table 2.4), OH and MTMOS have no effect on the original color of the facsimiles; however, the color increases slightly in value (reflectance) by treatment with a 5% w/v solution of MMA in toluene. When the samples are treated with either a sequence or a mixture of MMA and MTMOS, the color moves from a neutral to a more yellow color in hue, exhibits a slightly lesser reflectance as indicated by the decrease in value, and exhibits a slight increase in the strength of color as indicated by the increase in chroma.

Because independent applications of OH and MTMOS caused no change while MMA did cause a change, MMA also probably causes the color change in both the SQ and MX facsimiles. However, the SQ and MX color changes are not identical to that caused by MMA alone and, based on the available data, can only be attributed to the use of all three products in combination.

Because the stone of the convento column is of a different color, permeability, and geochemical composition than the facsimiles, this laboratory test can offer only a very approximate comparison of the effects of the different treatments on the color of the stone used on the convento column. As well, other factors may eventually alter the optical properties of treated stone by altering the optical properties of the conservation treatments; for instance, organic polymers such as MMA and MTMOS may be degraded over time by biological growths, photochemical processes, oxidation by oxygen and ozone, and attack by air pollutants. Cured OH is relatively more stable than MMA and MTMOS, but a slight discoloration has been noted after prolonged exposure to artificial UV and salt weathering (see Chapter 1 for a detailed discussion). Laboratory tests on the effects of aging in an external environment were outside of the scope of this study.

Other standardized tests have been developed to measure color and gloss which use less subjective instrumentation than the human eye; these include ASTM D 2244 - 89, "Standard Test Method for Calculation of Color Differences from Instrumentally Measured Color Coordinates," which employs a spectrophotometer or a colorimeter to evaluate differerences in color between a reference and a test specimen, and ASTM D 523 - 89, "Standard Test Method for Specular Gloss," which employs a glossmeter to measure specular gloss and/or the uniformity of the surface of a specimen. Instrumentation was not available to conduct these tests, but they would be useful in providing more data on changes in the appearance of the facsimiles and/or the convento column stone brought about by the conservation treatments. Too, if long-term or accelerated aging tests were conducted, the above procedures would help to produce more standard, and thus statistically comparable, results.

Based upon the results of ASTM D 1535 - 80, "Standard Method of Specifying Color by

the Munsell System," conservation treatments using either sequences or mixtures of MMA and MTMOS will probably cause a slight initial change in all aspects of the color of the stone. The color change remains constant whether MMA and MTMOS are applied in sequence or in mixture, thus one treatment cannot be recommended over the other based on the results of this test.

2.7.4 Water absorption

Standardized tests used

ASTM C 97 - 83 (Reapproved 1983), "Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone"

Purpose

To measure changes in the water absorption of the treated samples, and to determine if any differences in absorption rates resulted from the application of MMA and MTMOS in sequence rather than in mixture.

Significance

Changes in water absorption provide a measure of the water repellency imparted by the conservation treatments. Water is the catalyst for most of the deterioration mechanisms affecting the stone of the convento column, especially salt cycling, and a decrease in the water absorption of the treated surface signifies an increase in water repellency, thereby limiting the presence of water in the system and reducing the potential for deterioration.

Methodology

Because the tests required submersion in water, the cubes treated only with OH served as controls; thus a total of 12 facsimiles, all treated by partial immersion, were tested in accordance with the ASTM guidelines.

Results

The water absorption was determined for each facsimile (Appendix B, Table B.2) and then the mean value and standard deviation were calculated within each treatment group.

From the mean values, the % decrease in water absorption of the SQ and MX treatment groups in relation to the OH control group was also calculated (Table 2.5).

Table 2.5 Mean water absorption and % decrease with respect to the OH control sample

	OH	SQ	MX
mean (weight %) standard deviation	7.20 ±0.221	0.38 ±0.022	0.30 ±0.077
% decrease	0.00	95.0	96.0

The F-test and the t-test were used to statistically analyze the test results. Using the F-test, the standard deviations of the three treatment groups were compared to determine if there was any significant difference in the precisions of the results of each test group. A significant difference was found in the precision of the absorption test results between the treatment groups OH - SQ and SQ - MX, thus the results of the absorption tests for these pairs could not be compared using the t-test. However, no significant difference existed between the precisions of the OH and MX treatment groups; using the t-test, the means of these two groups were compared to determine if there were significant differences in water absorption. Significant differences between the means of the groups are recorded in Table 2.6.

Table 2.6 Significant differences in the water absorption of comparable treatment groups

treatment group	hypothesis test result
OH - SQ	not comparable
OH - MX	significant at 1% level of P
SQ - MX	not comparable

Discussion and Conclusions

Although changes in absorption between two of the three treatment groups are not statistically comparable using the t-test due to the magnitude of difference between standard deviations, a visual comparison reveals a tremendous decrease in the water absorption of facsimiles treated with SQ and MX. From the % decrease in mean absorption it is apparent that both the SQ and MX treatments impart a very high degree of water repellency to the facsimiles already treated with OH.

Because the standard deviations of the different treatment groups vary so widely, differences in the mean absorption of the SQ and MX groups could not be statistically compared using the t-test, therefore one treatment method cannot be recommended over the other upon the basis of these results. With a larger sample population, differences in the precisions (standard deviations) of the results might be reduced; then significant differences between the mean decreases in absorption imparted by the SQ and MX treatments could be measured. However, while the application of a mixture of MMA and MTMOS to a surface previously treated with OH can be recommended to significantly decrease the water absorption of that surface, the application of MMA and MTMOS in sequential order does not appear to augment or reduce the hydrophobic effects of the treatments.

2.7.5 Bulk specific gravity

Standardized tests used

ASTM C 97 - 83 (Reapproved 1983), "Standard Test Methods for Absorption and Bulk Specific Gravity of Dimension Stone"

Purpose

To measure changes in the bulk specific gravity of the treated samples, and to determine if any differences in bulk specific gravity resulted from the application of MMA and MTMOS in sequence rather than in mixture.

Significance

As discussed in Chapter 1.3, the greater the amount of a conservation treatment absorbed by a material, the greater the effectiveness of that treatment. Changes in bulk specific gravity provide a measure of the % retention of the conservation treatments.

Methodology

Because the tests required submersion in water, the cubes treated only with OH served as controls; thus a total of 12 facsimiles, all treated by partial immersion, were tested in accordance with the ASTM guidelines.

Results

The bulk specific gravity was determined for each facsimile (Appendix B, Table B.2) and then the mean value and standard deviation were calculated within each treatment group. From the mean values, the % increase in bulk specific gravity of the SQ and MX treatment groups in relation to the OH control group were also calculated (Table 2.7).

Table 2.7 Mean bulk specific gravity and % increase with respect to the OH control sample

	OH	SQ	MX
mean	2.10	2.14	2.19
standard deviation	±0.008	±0.015	±0.019
% increase	0.00	1.90	4.30

The F-test and the t-test were used to statistically analyze the test results. Using the F-test, the standard deviations of the three treatment groups were compared to determine if there was any significant difference in the precisions of the results of each test group. No significant difference existed between the precisions of any treatment groups; using the t-test, the means of these pairs were compared to determine if there were significant differences in the bulk specific gravity of the different treatment groups. Significant differences between the means of the groups are recorded in Table 2.8.

Table 2.8 Significant differences in the bulk specific gravity of comparable treatment groups

treatment group	hypothesis test result
OH - SQ	significant at 1% level of P
OH - MX	significant at 1% level of P
SQ - MX	significant at 1% level of P

Discussion and Conclusions

All of the results of the bulk specific gravity test are comparable and all of treatment groups show significant differences at the 1% level of probability. The facsimiles treated

with MX display the greatest increase in bulk specific gravity, thus the greatest percent absorption of the MMA and/or MTMOS treatments. As previously discussed (Chapters 1.5.4 and 2.7.1), the polymer network formed by MMA may "entrap" the MTMOS, preventing its evaporation, promoting *in situ* condensation reactions, and thus increasing the amount of MTMOS deposited in the samples. Also, MMA is known to significantly decrease the porosity of stone (Chapter 1.4); the capacity of the facsimiles to absorb MTMOS after the polymerization of MMA would be much reduced. These two factors may explain the lesser increase in bulk specific gravity exhibited by the SQ treatment group. Based upon these test results, a sequential application of MMA and MTMOS would not result in as high a percent absorption of conservation materials, and would be less effective than a mixed application.

2.7.6 Water vapor transmission

Standardized Tests Used

ASTM E 96 - 90, "Standard Test Methods for Water Vapor Transmission of Materials," Water Method

Purpose

To measure any significant change in water vapor transmission (WVT) rates caused by conservation treatments using OH, MMA, and MTMOS in relation to untreated samples, and to determine if any significant differences in water vapor transmission rates resulted when MMA and MTMOS were applied in sequential order as opposed to a mixture.

Significance

Ideally, a conservation treatment would not alter the physical characteristics of the treated stone, including its rate of water vapor transmission. When water is a principal agent in the deterioration of the stone, it is necessary to increase the water repellency of the stone if water cannot be removed from the deterioration cycle. But it is equally necessary to ensure that any water which does enter the stone, whether by direct contact or condensation, is also able to evaporate at a reasonable rate. Water trapped within the stone will fuel water-related weathering mechanisms and hasten the deterioration of the stone. Thus the lesser the decrease in the water vapor transmission rate, the more easily water and water vapor will exit, and the better the conservation treatment.

Methodology

A total of sixteen disks treated by partial immersion were tested, four each of CT, OH, SQ, and MX. The samples measured 2.75" in diameter and were 0.75" thick, with a

surface area of 5.94 in^2 per side.

130 ml of deionized water were poured into 250 ml disposable plastic beakers and samples were then sealed to the mouths of the beakers with microcrystalline wax. The beakers of four samples (one each of CT, OH, SQ, and MX) contained no water; these served as "dummy specimens" and were used to compensate for variability in testing conditions. The assemblages were then placed on racks in a glass tank, over which a glass lid was sealed using Dow Corning High Vacuum Grease. Trays of Drierite, an anhydrous calcium sulfate dessicant, were placed in the tank beneath the samples, maintaining a relative humidity of 37 ± 3% in the tank. Temperature was more difficult to control and ranged from 20 - 27°C. Measurements of relative humidity and temperature in the tank were taken twice a day. Samples were weighed on a scale with a sensitivity of 0.01 g once a day at least four times a week until the vapor transmission rate was established. Because the scale slipped from calibration easily, a 295.0g weight was weighed on the scale prior to the weighing of the samples; the data collected each day was corrected by adding or subtracting the error in the weight of the 295.0 g weight.

The weight measurements of the samples were recorded and then corrected using the dummy specimens as recommended by ASTM E 96 - 90. The dummy specimens within each treatment category (CT, OH, SQ, MX) exhibited very different daily weight fluctuations. Thus the weight of each "real" specimen was corrected by adding or subtracting the daily weight change of the dummy specimen within its treatment category, and not an average of the weight fluctuations of all of the dummy specimens for that day (e.g., the weight changes of specimens V10.SQ - V12.SQ for a given day were corrected by adding or subtracting only the weight change of dummy specimen V9.SQ for that day, and not the median change of all four dummy specimens) (Appendix B, Table B.3).

Results

The daily rate of water loss due to vapor transmission (WVT, expressed in g/h·m2) was determined for each facsimile, and then the mean value and standard deviation were calculated within each treatment group. From the mean values, the % decreases in the WVT rates of the treated samples in relation to the untreated control sample were also calculated (Table 2.9).

Table 2.9 Mean WVT rate and % decrease with respeet to the untreated control sample

	CT	OH	SQ	MX
mean (g/h·m2) standard deviation	7.67 ±0.852	4.33 ±0.187	2.15 ±0.307	2.54 ±0.129
% decrease	0.0	44.5	72.0	66.9

The F-test and the t-test were used to statistically analyze the test results. Using the F-test, the standard deviations of the four treatment groups were compared to determine if there was any significant difference in the precisions of the results of each test group. A significant difference was found in the precisions between the treatment groups CT and OH as well as CT and MX, thus the results of the WVT tests for these pairs could not be compared using a t-test. However, no significant difference existed between the precisions of CT and SQ, OH and SQ, OH and MX, and SQ and MX; using the t-test, the means of these pairs were compared to determine if there were significant differences in the WVT rate of the different samples. The levels of probability of significant differences between the means of the sample groups are reported in Table 2.10.

Table 2.10 Significant differences in the mean WVT rates of comparable treatment groups

treatment group	hypothesis test result
CT - SQ	significant at the 5% level of probability
OH - SQ	significant at the 5% level of probability
OH - MX	significant at the 5% level of probability
SQ - MX	not significant

Discussion and Conclusions

Although some of the data is not statistically comparable using a t-test due to the significant differences in precision between the treatment groups, a visual comparison of the means reveals that all of the treatments, OH, MX, and SQ, affect the water vapor transmission rate of the facsimiles; indeed, the decreases in WVT are quite large and well above any recommended limits for conservation materials. The significant differences between the OH group and both the SQ and MX groups indicate that OH is not solely responsible for the decrease, and that sequences and mixtures of MMA and MTMOS respectively contribute to the decrease in WVT by approximately 75% and 50% of that caused by the OH alone.

Of greatest interest in this test is the fact that the decreases between WVT rates caused by the method of treatment, namely the application of MMA and MTMOS in sequence or in mixture, statistically showed no significant difference. On the basis of this test, a sequential application could be considered as effective as a mixture. But it must be noted that a difference does exist between the means of SQ and MX and that the sample number used to establish each mean was small (3). Further WVT tests using a larger sample pool may reveal a significant difference between the means of the two treatment methods; a

larger sample pool might also allow for comparable precisions between the untreated control group and all of the treated groups.

Also of importance, the treatment groups used in the WVT test do not reveal the extent to which MMA and MTMOS, whether independently or in sequence or in mixture, affect the WVT in the absence of OH. Further WVT tests incorporating these treatment groups would allow for a more accurate understanding of the potential effects of both the conservation materials and the treatment methods on the water vapor transmission of the conserved object.

2.7.7 Resistance to salt crystallization

Standardized tests used

ASTM C 88 - 90, "Standard Test Method for Soundness of Aggregates by Use of Sodium Sulfate or Magnesium Sulfate"

RILEM 25 P.E.M. Test V.1b, "Crystallisation Test by Total Immersion (for Treated Stone)"

Purpose

To measure the relative resistance to deterioration by salt crystallization of facsimiles conserved with the OH, SQ, and MX treatments, and to determine if any significant differences in resistance to salt crystallization resulted when MMA and MTMOS were applied in sequential order as opposed to a mixture.

Significance

Salts were the primary cause of deterioration of the convento column stone and the complete removal of salts from the system was not practicable. An effective conservation treatment would optimally inhibit salt cycling or would allow for the removal of salts after treatment. In the long term, the treatment would also have to perform well in the presence of on-going cycling by providing improved intergranular cohesion and microcrack adhesion.

Methodology

Twelve cubes treated by partial immersion were tested following the ASTM guidelines. A single salt solution was prepared using anhydrous sodium sulfate; this solution was reused for each cycle. Samples were then cycled over a 24 hour period, undergoing 16-

18 hours immersion in the salt solution, followed by 4-5 hours of oven drying and two hours of cooling. Weight measurements were taken immediately after removal from the oven (Appendix B, Table B.4). Oven temperature was maintained at 60 ± 5°C as recommended in the RILEM test; the samples had been treated with organic materials and their properties might have been altered at the high drying temperature (105°C) recommended in the ASTM test.

Results

The expression of results is in accordance with the RILEM test. The mean weight loss of the facsimiles as a percentage of the original weight was calculated after 15 and 18 cycles (Table 2.11). One of the OH samples was destroyed after 7 cycles and the remaining 3 sampies after 8 cycles, while none of the SQ or MX samples were completely destroyed after 18 cycles, at which point the test was concluded (Figure 2.12).

The qualitative manner in which the facsimiles resisted salt cycling was also of importance. To determine this, the mean weight loss (% of original weight) was calculated for each treatment category after each cycle. The results were graphed and the curves compared in order to determine qualitative differences, if any, in the ways in

Table 2.11 Mean weight loss of facsimiles after 15 and 18 salt cycles

# of cycles	mean weight loss (% original wt)		
	OH	SQ	MX
15	100.0	9.5	8.9
18	100.0	28.4	41.2

Figure 2.12 Appearance of facsimiles S5.OH - S8.OH after 8 cycles of salt crystallization, and appearance of facsimiles S9.SQ - S12.SQ and S13.MX - S16.MX after 16 cycles of salt crystallization.

which the different treatments deteriorated through repeated salt cycling (Figures 2.13a and 2.13b).

Discussion and conclusions

As illustrated in Table 2.11, facsimiles treated only with OH were quickly destroyed by repeated immersions in the salt bath, although they displayed marked improvement over untreated CT facsimiles, which disintegrated upon contact with water. In contrast, the percent weight loss for groups treated with SQ and MX is very minimal through cycle 15, and the ultimate destruction of the facsimiles is much slower than that of the OH or CT samples (see Figure 2.12). In part, this may be a result of the consolidating properties of ethyl silicate (as observed in the improved resistance of the OH group over the CT group)

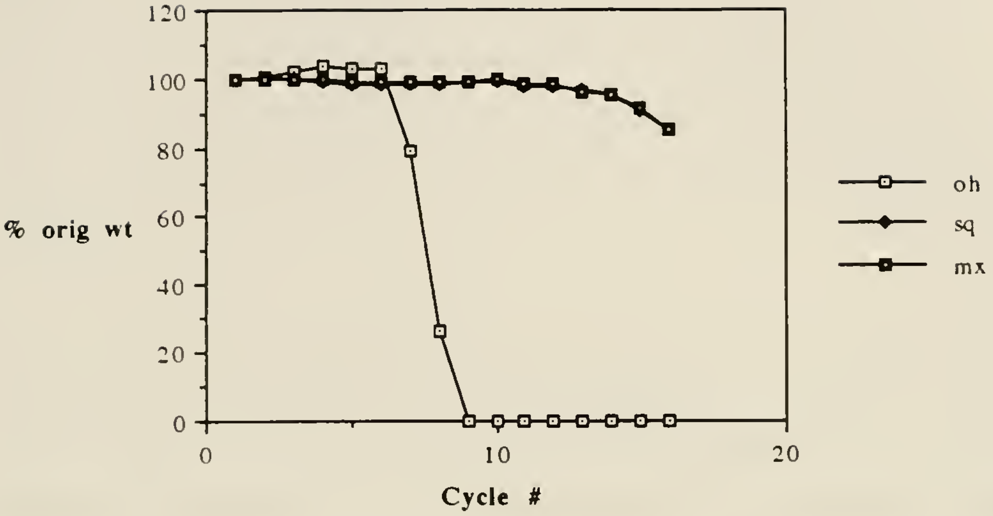

Figure 2.13a Resistance of treated facsimiles to salt crystallization, expressed as mean % of original weight. At this scale, data for SQ and MX samples nearly coincide.

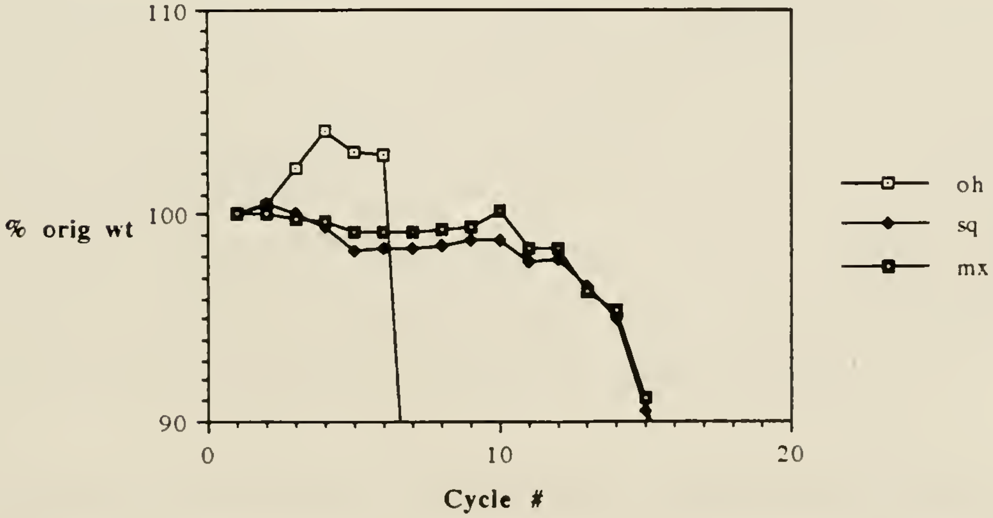

Figure 2.13b Detail, resistance of treated facsimiles to salt crystallization, expressed as mean % of original weight.

and MMA. However, the addition of the water-repellent (MTMOS) reduces the facsimiles' absorption of water by about 95% (Chapter 2.7.4). By drastically reducing the presence of the catalyst (water) in the salt crystallization system, the MTMOS limits the extent of salt solubilization and recrystallization and possibly even delays its inception. Thus the excellent resistance of the SQ and MX groups to destruction by salt cycling is probably a result of the addition of the water repellent to the conservation treatments.

The mean resistance of the SQ and MX treatment groups remain about the same through cycle 15, but by cycle 18 the MX treatment group has lost almost 33% more weight than SQ group. The precisions of mean weight losses between the SQ and MX treatment groups vary too widely to be statistically compared; a larger sample population might allow for comparable results, but at this point no conclusions can be drawn from the more rapid decline of the MX sample population after cycle 15.

Qualitatively, the three treatment groups displayed different resistance patterns to salt crystallization. In Figure 2.13a, the resistance patterns of the SQ and MX groups coincide almost exactly. Initially, both MX and SQ lose a little weight (1%) and then maintain equilibrium until cycle 13, at which point they begin to gradually lose weight. In contrast, the OH group, without the inhibiting water repellent, immediately exhibits an increase in weight and then an exponential deterioration after cycle 6. This weight gain is caused by the increased presence of salt crystals within the facsimiles.

The greater detail of Figure 2.13b reveals subtleties in the mean resistance patterns of the SQ and MX treatment groups. Initially, both gain fractional amounts of weight and then lose weight until an equilibrium is approached after cycle 5. Minor weight increases

ensue until cycle 12, when both groups begin to lose significant amounts of weight. The MX group exhibits a weight gain just prior to decline, albeit much smaller than that exhibited by the OH group, while the SQ group does not.

Based upon the results of this test, it appears that no significant differences in the resistance of the facsimiles to salt crystallization are caused by the use of MMA and MTMOS in sequence as opposed to mixture. However, the dramatic increase in resistance of both the SQ and MX groups over that of the OH group provides a strong argument for the use of MMA and MTMOS in conservation treatments where salt cannot be removed from the affected stone. This increase in resistance is most likely a result of the water-repellent properties imparted by the MTMOS and to a lesser extent the consolidating properties of the MMA. The exact contribution of each conservation material to the improved resistance cannot be determined without further testing.

2.8 Conclusions

The results of the experimental program revealed several significant differences between untreated facsimiles, facsimiles treated with sequences, and facsimiles treated with mixtures. A comparison between untreated and treated groups revealed that both sequences and mixtures of MMA and MTMOS caused a negative change in color and a significant decrease in the water vapor transmission rates of the facsimiles. Positively, the water absorption rates of the treated groups was dramatically reduced and their resistance to salt crystallization greatly improved.

A comparison between sequential and mixed applications of MMA and MTMOS revealed no significant differences in color change, water absorption, water vapor transmission, or resistance to salt crystallization. However, mixtures of MMA and MTMOS exhibited a greater mean depth of penetration than sequences, and facsimiles treated with mixtures exhibited a greater mean increase in bulk specific gravity than those treated with a sequence. The microstructures resulting from the two treament methods differed greatly: the mixture formed a uniform, smooth, and continuous surface coating while the presence of MMA and MTMOS were barely discernible when applied in sequence. The resultant film resembled that of OH alone, which was discontinuous and inhomogeneous. Because of the limited number of samples examined, these last results were felt to be inconclusive.

Because mixtures exhibited a greater depth of penetration and percent retention of MMA and MTMOS, the sequential application of MMA and MTMOS was felt to be somewhat less effective. However, there were no significant differences in any of the other performance criteria for which the two treatment methods were tested. To determine the

appropriate treatment for the convento column at Mission San José y San Miguel de Aguayo, these conclusions were considered in combination with both the deterioration patterns and the other treatment requirements of the stone (Chapter 3.5).

2.9 Recommendations for future research

Further research through experimentation would help to clarify differences in the effectiveness of sequential and mixed applications of acrylics and silanes. Tests already conducted in this program could be made relevant for specific types of stone by applying them to weathered stone samples rather than to facsimiles. Also, by increasing the size of the sample pools, the standard deviation of the experimental results could be reduced and the data rendered more statistically comparable.

Other tests which were not included in this experimental program would also help in the evaluation of the relative effectiveness of sequential and mixed applications of MMA and MTMOS. In particular, tests measuring the consolidating effects of the two treatment methods would be useful, including measurements of changes in the abrasion resistance, compressive and tensile strength, and modulus of rupture of treated samples. Too, exposures to UV radiation and acid fog would reveal if any differences in aging were caused by the method of application and the resultant differences in morphology of sequences and mixtures of MMA and MTMOS.

Examination of different layers of the treated samples using scanning electron microscopy might reveal whether any segregation or separation of the two elements was caused by either method of application. Also, the examination of samples at each stage of a sequential treatment would reveal to what extent the treatments affected each other. Gas

chromatography could be used to characterize the chemical interactions of MMA and MTMOS when applied in a sequence, similar to the way in which Wheeler et al. (1991) characterized the chemical interactions of MMA and MTMOS when applied in mixtures. Using this technique, one could determine whether MMA is resolubilized and lost to evaporation when MTMOS is applied as the second step in a sequence, and also whether MTMOS is "entrapped" by the cured MMA and/or to what extent MTMOS too is lost to evaporation.

In any future testing of mixtures and sequences, the removal of ethyl silicate (OH) from the treatment program would allow for a clearer evaluation of the effects of MMA and MTMOS on the properties of treated samples. The testing of sample groups treated with MMA only and MTMOS only (in concert with sample groups treated with sequences and mixtures) would also increase the understanding of the roles of the individual materials in the alteration of the physical and mechanical properties of a treated stone.

Chapter 3. Case Study: Conservation of the Column in the Convento of Mission San José y San Miguel de Aguayo, Texas

3.1 Overview

The conservation of a deteriorated limestone column in the convento of Mission San José y San Miguel de Aguayo was undertaken through a cooperative agreement between the Architectural Conservation Laboratory of the University of Pennsylvania and the Southwest Regional Office of the National Park Service. The drums of the column appear to have been originally bedded in gypsum-based mortar (hydrated calcium sulfate), and gypsum patches had been applied in subsequent repair campaigns. The column is an exterior architectural element, and its rapid deterioration was caused by the repeated solubilization and recrystallization of the calcium sulfate in the pores of the stone. The prevalent types of deterioration exhibited by the stone were loss of intergranular cohesion (friability), microcracking, and flaking. To reestablish intergranular cohesion, an ethyl silicate (OH) was chosen as the consolidant because of its relatively good depth of penetration. An acrylic (MMA) was chosen for its consolidative and adhesive properties while an alkyl alkoxysilane (MTMOS) was chosen for its consolidative and water repellent properties.

The results of the pretreatment experimental program (Chapter 2) indicated that the application of MMA and MTMOS in a mixture, rather than in sequential order, would be somewhat more effective for the adhesive consolidation and protection of the stone. The two types of treatments were then considered in conjunction with the particular conditions

and treatment requirements of the column. The localized deterioration and the need to infill large areas of loss after consolidation spoke against the use of a mixture, and it was decided to employ a sequential application of MMA and MTMOS because of its greater flexibility and potential effectiveness under the circumstances.

The final conservation plan for the convento column included preconsolidation with MMA, desalination, consolidation with OH, infilling with a hydraulic-lime-based material, and protection with a water repellent (MTMOS). These treatments were applied in four phases over a period of five months. A maintenance plan was designed to monitor the effectiveness of treatments and ensure the continued protection of the column.

3.2 Introduction to the case study

The Architectural Conservation Laboratory of the University of Pennsylvania and the Southwest Regional Office of the National Park Service undertook a joint research, training, and treatment program on the conservation of weathered sandy limestone at the convento of Mission San José y San Miguel de Aguayo, San Antonio Missions National Historical Park, San Antonio, Texas. The project, conducted under a cooperative agreement established in 1992 between the University and the National Park Service, provided thesis research and practical conservation training. Funding was provided by the friends' group, Los Compadres de San Antonio Missions National Historical Park, which secured a grant from the Marcia and Otto Koehler Foundation. The project was undertaken from January to May of 1993. Team members for the project included: Frank G. Matero (University of Pennsylvania) and Jake Barrow (National Park Service, Southwest Regional Office), project directors; Anne Brackin (University of Pennsylvania), Keith Newlin (National Park Service, Denver Service Center) and Diana

Motiejuanaite (National Park Service, ICOMOS intern), project interns.

Training components included on-site participation by team members and presentations at the midpoint and conclusion of the project to members of the National Park Service, Los Compadres de San Antonio Missions National Historical Park, the Koehler Foundation, the local chapter of the American Institute of Architects, and other interested parties. As well, team members will be applying the methodology and treatments learned at Mission San José to future projects both within and outside of the National Park Service system.

3.3 History of the site

Mission San José y San Miguel de Aguayo was founded in 1721 by the Franciscan brothers of the College of Zacatecas in Zacatecas, Mexico. A series of buildings were erected to house the activities of the mission through the years, but in the 1770s an extensive rebuilding program was undertaken, resulting in many of the elements of the church and convento complex standing today. The rubble walls of the new buildings were constructed mainly of local calcareous tufa and impure limestone (containing a high percentage of quartz sand) and were laid in a lime mortar; carved elements were sculpted of a softer and more compact white limestone.

By the 1820s, the mission was nearly abandoned, and by the 1850s was considered a picturesque ruin by tourists and photographers. In 1861, the church and convento were reinhabited by brothers of the Benedictine order, and a program of rebuilding was begun using locally available raw materials. In the convento, the northern and southernmost walls of the two-story structure extending east from the church were retained; however, the remaining internal partition walls were demolished and replaced. Most of the new

elements were rubble laid in lime with the exception of the brick voussoirs of the lancet-arched openings and the carved, octagonal, sandstone drums of the column on the second story of the east-west interior wall. The drums were laid in gypsum mortar. These rebuilt elements of the convento were meant to serve as interior spaces, with the column accenting the second story of a stair hall; however, in 1868 the Benedictines were forced to abandoned the site, and the convento was never roofed.

Following the efforts of the Benedictines, the mission complex was again largely abandoned until the 1920s, when renewed interest in all of the San Antonio missions resulted in extensive archaeological investigation, reconstruction, and maintenance of the structures. In conjunction with these efforts, the convento of Mission San José was stabilized and the column bears the evidence of two patching campaigns. The first is revealed in a photograph from around 1927 in which large white patches are visible (Figure 3.1); these match the locations of the present-day gypsum patches. The second set of patches were applied at an undetermined later date, and appear in photographs dating from the 1960s; these are of lime and sand, and overlay the earlier gypsum patches and original gypsum bedding mortar (Figure 3.2).

In 1978, San Antonio Missions National Historical Park was established. Since 1987, the increasingly rapid deterioration of the column in the convento has been monitored by the National Park Service, leading to the decision to conserve the column and ultimately to the design and execution of this conservation program in the spring of 1993.

3.4 Pretreatment conditions

In plan, the column is an elongated octagon, approximately 18" on its east-west axis and

Figure 3.1 Southeast elevation of the convento column circa 1927 (courtesy Special Library, San Antonio Missions National Historical Park, San Antonio, Texas).

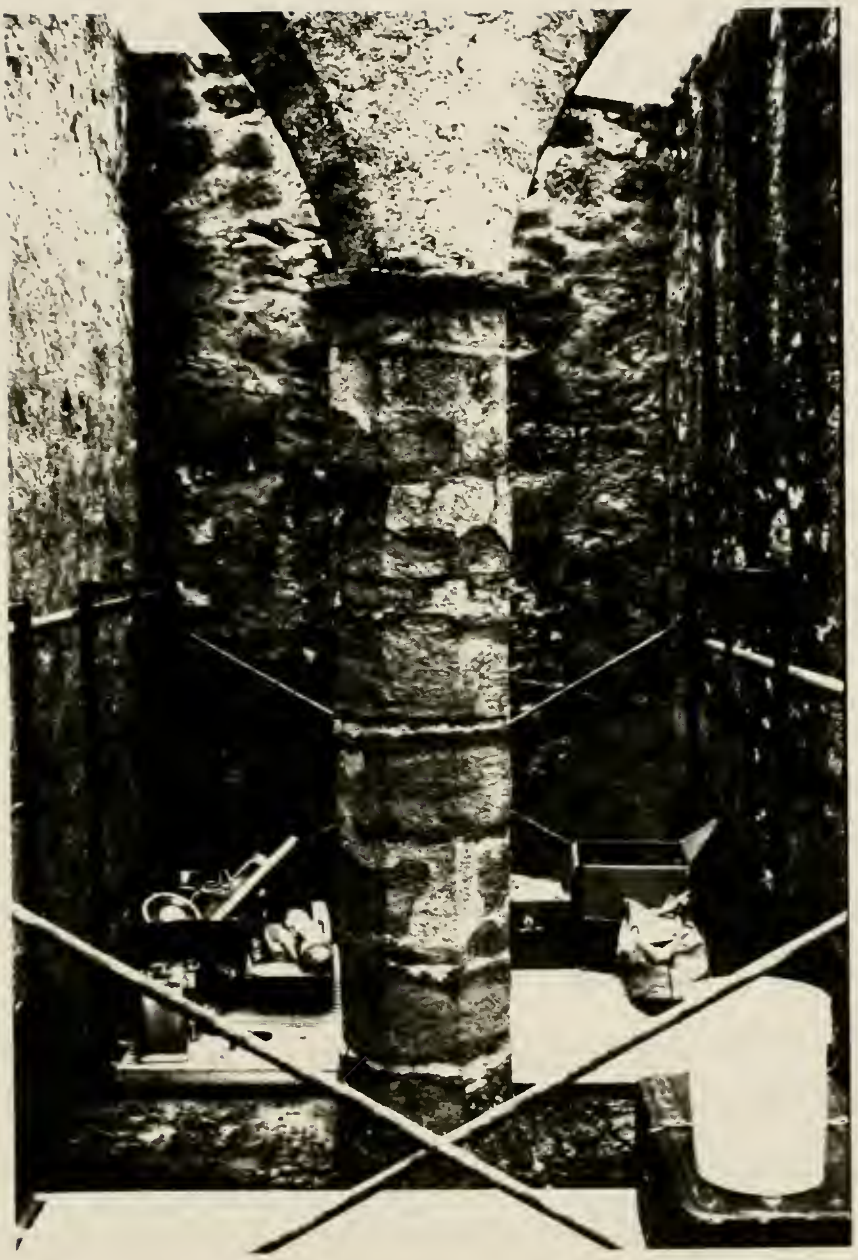

Figure 3.2 South elevation of convento column before conservation, January 1993.

24" on its north-south axis. It is composed of nine drums reaching a height of 7' 10"; the first seven drums from the base are carved from a golden-brown sandstone, and the eighth from a weaker grey limestone. The ninth drum forms a simple capital, and is also of a golden-brown sandstone. Horizontal joints between range from 1/8" to 3/4", varying with irregularities in the drums; the larger joints are chinked with tabular stones. The second, fourth, and sixth drums are composed of two parts, with vertical header joints on the east-west axis; these joints range from 1" to 4" and are packed with cobbles. The east and west faces of all drums are 1' 1" in width; all other faces are 7.5" in width. Two independent mineralogical and petrographic analyses of stone samples from the convento column have been conducted (Chapter 2.2). Both analyses indicate that the stone is an impure limestone, composed of a high percentage of angular grains of quartz in a cryptocrystalline calcite matrix.

The condition of the column prior to conservation was quite poor. Levels of deterioration were localized, with the most extensive found in areas immediately beneath and adjacent to gypsum mortar and patches; stone in these areas was very friable to the touch and exhibited extensive microcracking and flaking. The sound cores beneath deteriorated surfaces were between 2 - 5 cm from the surface. The southern faces of the column were relatively sound, as were isolated areas on other faces. No gypsum was used above the capital of the column and this drum remained in excellent condition. Many patches of lime and gypsum rang hollow when tapped, indicating poor attachment to the underlying stone. When these patches were subsequently removed, the stone beneath was found to be severely deteriorated. A complete list and description of pretreatment conditions is provided in Appendix C; graphic documentation of pretreatment conditions is contained in the final project report prepared for San Antonio Missions National Historical Park, Southwest Region, National Park Service (Brackin, 1993).

The use of calcium sulfate (gypsum) as both a bedding mortar and a patching material was determined to be the probable cause for this massive deterioration (Chapter 2.2). Photographs from 1927 show that the profiles of the column drums were largely intact after almost 150 years of weathering (see Figure 3.1); they also show that large patches had been applied which correspond to the present location of the gypsum. The extensive deterioration which has occurred in the past 60 years indicates that these gypsum patches are probably responsible. The presence of clays and iron oxides in the mineralogical composition of the stone may also be contributing to deterioration. In the presence of water, clays swell and exert pressure within the stone pores similar to gypsum. In like manner, iron ions may change oxidation states in the presence of water; the crystal structure of the new oxides may take up more volume than the original oxides.

3.5 Column treatment

Deteriorated areas of the column required a deeply-penetrating consolidant to reestablish intergranular cohesion, an adhesive to bridge microcracks and reattach loose flakes, and a water-repellent to minimize the deterioration caused by the presence of water in the stone. Because the zone from the deteriorated surface to the sound core of the stone was so wide, an ethyl silicate (OH) was chosen as the consolidant. This choice was based upon the knowledge that ethyl silicates provide greater depth of penetration than other commonly-used consolidants for stone, including epoxies, acrylics, and mixtures of ethyl silicate/methyl triethoxysilane and acrylic/methyl trimethoxysilane. However, ethyl silicate cannot bridge gaps between cracks or large grains of stone, nor does it possess water-repellent properties (Chapter 1.4.1). To achieve this type of consolidation and protection, mixtures of acrylics (MMA) and silanes (MTMOS) are commonly employed in stone conservation (Chapter 1.6).

But after consolidation, large areas of loss were designated to be infilled with a patching material to restore the visual coherence and the structural integrity of the column. While it was necessary to stabilize the friable surfaces with both a consolidant and an adhesive prior to infilling, a hydrophobic surface (which would result from the use of a mixture) would interfere with the adherence of patching materials. The incorporation of epoxies or acrylics in the patching material would allow for successful application over a water-repellent surface (Larson, 1982). However, these organic resins are susceptible to degradation by UV radiation; the column is an exterior architectural element and it was more desirable to use a stable inorganic infill material, such as the hydraulic-lime-based patches which were proposed for use.

Also considered was the fact that the deterioration of the column was localized in association with gypsum mortars used in joints and as patches. Relatively sound areas would benefit from the improvement in mechanical properties imparted by ethyl silicate and from the protection imparted by a water-repellent, but the use of adhesives was not necessary. Applications of OH and silanes would not significantly alter the appearance of the stone, but the application of a mixture of an acrylic and a silane would unnecessarily introduce the adverse effects of color change and reduction of water vapor permeability known to be caused by acrylics (Chapter 1.5).

In the pretreatment experimental program, mixtures exhibited a greater depth of penetration and percent retention of MMA and MTMOS, the sequential application of MMA and MTMOS was felt to be somewhat less effective (Chapter 2). However, there were no significant differences in any of the other performance criteria for which the two treatment methods were tested. To determine the appropriate treatment for the convento column at Mission San José, these conclusions were considered in combination with both

the deterioration patterns and the other treatment requirements of the stone as discussed above.

A sequential application of the consolidant, adhesive, and water repellent was considered more practical, flexible, and potentially more effective than a mixed treatment under these particular circumstances. Also in support of its selection was the fact that, in deteriorated areas designated for infill, the application of the acrylic would not be followed by the application of a water repellent; instead infills would be applied directly over the consolidated surfaces, and then the water repellent would be applied. This method would eliminate the reduction in MMA and MTMOS deposition found to be caused by a sequential application (Chapter 2.7.2). Thus it was decided to implement the following conservation plan, which consisted of sequential steps and did not involve the use of a mixture of an acrylic and an alkyl alkoxysilane:

- preconsolidation of fragile surfaces and application of wet-strength tissue paper to vulnerable flakes with an acrylic (MMA) to allow for desalination and grouting of large voids without further loss of material
- application of consolidant (OH) to all surfaces of the column
- application of adhesive (MMA) to all areas exhibiting friability and microcracking
- application of hydraulic-lime-based patching material in designated areas
- application of water repellent (MTMOS) to all surfaces of the column, including areas of infill

Conservation of the column in the convento of Mission San José was phased to coincide with four separate trips to the site by members of the team. Treatments began in February

and ended in May of 1993.

3.5.1 Phase 1: Preconsolidation and desalination

Scaffolding was erected and a tarpaulin set up to protect the column from inclement weather during treatment. Complete photographic documentation using 35 mm color and black and white film ensued, as well as written documentation and a graphic conditions survey (Brackin, 1993). Previous repairs using lime and gypsum patching were removed. At this time it was discovered that the drums of the column had been laid and head joints filled with a gypsum mortar; because this gypsum was contributing to deterioration as previously discussed, the joints were taken back as far as possible.

Facings of Japanese tissue paper were applied to protect fragile areas, using 7.5 - 15 % solutions of an acrylic resin (Acryloid B72) in a 1:1 mixture of xylenes and toluene.[1] Fine cracks were injected with a 15 % solution. All other friable surfaces were preconsolidated with the same solution applied in increasing strengths from 3.75 - 7.5% so that the poultices used in desalination could be applied without significant loss of material.

Large voids exposed during patch removal were grouted using a mixture of 2:1:1:1.5 (by volume) of hydraulic lime, microballoons (Zee-lite spheres), fine silica sand (passing a #30 seive), and water; the grout was injected using syringes and a 10-gauge canula.[2] The

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[1] Acryloid B72 is manufactured by Rohm and Haas, Philadelphia, PA, but is available only through distributors. It is a copolymer of ethyl methacrylate and methyl acrylate with a 70:30 molar ratio (Horie, 1990).

[2] Riverton hydraulic lime is manufactured and sold by the Riverton Corporation, Riverton, VA, 22651, (800)336-2490. Z-lite spheres are manufactured and sold by Zeelan Industries, Inc., 141 East 4th St. #220, St. Paul, MN, 55101-1620, (612) 292-9271.

poultice used for desalination was a mixture of ground and macerated 1/2 rag stuff paper pulp and 3% glycerin. Three separate poultices were applied over the next month.

3.5.2 Phase 2: Consolidation

All Japanese tissue paper and cotton used during preconsolidation and grouting were removed from the column using toluene, metal spatulas, and dental picks. The column was then consolidated using four gallons of ethyl silicate (Conservare Stone Strengthener OH), applied with a low-pressure sprayer. A gallon of methyl ethyl ketone (Stone Strengthener Solvent) was then sprayed on all surfaces to remove any surface accumulation of ethyl silicate.[3] After drying overnight, the column was wrapped in an electric blanket and swathed in plastic sheeting to protect it from freezing and wet weather while the ethyl silicate cured.

3.5.3 Phase 3: Patching

In preparation for patching, a 15 % B72 solution was injected behind flakes and into cracks to achieve final reattachment. Larger cracks, too narrow for grouting, were injected with a 1:1 mixture of 15 % B72 solution and microballoons. Faces which were still too unsound to support the weight of the fills were taken back to sound material using a tooth chisel; no surfaces displaying original tooling were affected. To create integral keys for the fills, 1/2" - 1" deep holes were drilled into the newly exposed surfaces in a random pattern (approximately 1" - 2" apart) using a 1/2 inch masonry bit.

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[3] Conservare Stone Strengthener OH and Stone Strengthener Solvent are manufactured and sold by ProSoCo, Inc., PO Box 171677, Kansas City, KS, 66117, (913) 281-2700.

Scratch coats of patching material were applied to the prewetted surface of the column and into the drilled holes, consisting of a 1:3 mixture (by volume) of hydraulic lime and local mason's sand. When "thumbprint dry," the coats were scored and more material was applied; this was repeated until surfaces were built out roughly to 1/4 inch back from original surfaces. Finish coats of a 1:3 mix of sieved hydraulic lime and yellow bar sand colored with alkali-stable masonry pigments (raw and burnt sienna from Rainbow and Germantown lamp black), which had been prepared and prematched at the Architectural Conservation Laboratory, were then applied flush with the original faces. After drying overnight, the patched surfaces were worked into plane and recessed from the remaining original surfaces to differentiate the repair from the original surface; joint lines were scored with a narrow stick to reestablish the original drum configuration. A slurry of the finish coat was worked into all small cracks on the original surfaces to prevent the ingress of water. Inclined mortar copings were installed on the top of the column capital and at the bases of the east and west elevations to facilitate the shedding of water at these critical junctures; the copings are not visible from the ground. Lastly, stone surfaces were brushed with a 10 % acetic acid solution to remove any lime residue.

3.5.4 Phase 4: Application of water repellent

After curing for one month, the new fills were roughened with a stiff bristle brush and the laitence from the lime removed with acetic acid solutions ranging from 5% - 20%. To unify the various patches while breaking their monotony, a dilute color wash of Liquitex permanent acrylic watercolors (equal parts raw umber and raw sienna in water) was spattered and dabbed over the surface of the patches using a stiff bristle brush.

Using a 1/4 inch masonry bit, randomly-spaced half-inch holes were drilled into original

surfaces which still rang hollow. A solution of 15% B72 in toluene and a mixture of 1:1 15% B72 and microballoons were injected into these holes to readhere the detached surfaces. Unfilled hairline cracks were also injected with the 15% solution. Patching material was applied to minor areas which had been overlooked and to the mortar coping atop the capital to increase the angle and facilitate water runoff.

The protective tarp sheltering the column was removed and the column was allowed to dry in the sun. After drying, 32 ounces of a full-strength solution of a methyl trimethoxysilane monomer (Dow Corning Z6070) were brushed over the surface of the column to impart water repellency.[4] Final documentary photographs in 35 mm black and white print and color slide film were taken of the column (Figure 3.3).

3.5.5 Maintenance

The deterioration mechanisms of the column are inherent in its mineralogical composition and in its construction. Because it was not possible to remove all gypsum from the stone, it was not possible to amend these mechanisms entirely. However, water is the requisite catalyst and by ensuring water repellency, deterioration can be slowed.

A program of preventive maintenance for the column involves monitoring the water repellent coat and periodically replacing it. The water repellent coat is expected to last from five to seven years; to monitor its effectiveness, annual permeability measurements should be taken using the Rilem water absorption test. Readings should be taken from

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[4] Dow Corning Z6070 is manufactured by Dow Corning Corp., PO Box 997, Midland, MI, 48686-0997, (800) 248-2481, and is available through distributors. It is a monomer of methyl trimethoxysilane.

both original surfaces and from patched areas because these surfaces may weather differently. The initial locations from which the readings are taken should be recorded and remain constant from year to year. When a notable increase in permeability occurs, a new water repellent should be applied. Undiluted Dow Corning Z6070 should be brushed onto all surfaces; if this product is not available, another commercial methyl trimethoxysilane product may be substituted.

If salt efflorescences reappear on the surface of the stone or the infills, or if deterioration patterns associated with salt weathering are noted, the salts may be removed using the above described technique (Chapter 3.5.1) or using standard poulticing procedures described in the conservation literature. The column may also be retreated with any or all of the materials used in this conservation program.

3.6 Conclusions

The conservation treatment of the convento column at Mission San José, using an ethyl silicate conslidant followed by sequential applications of methyl methacrylate and methyl trimethoxysilane, was successful. The use of the materials in sequential order allowed for flexibility in treating stone which exhibited only localized deterioration, and also permitted the subsequent application of infills. More time must elapse before the aging of the treatment can be evaluated, but after one year, no alteration or new deterioration was visible on either the stone or the infills of the column (Matero, personal communication).

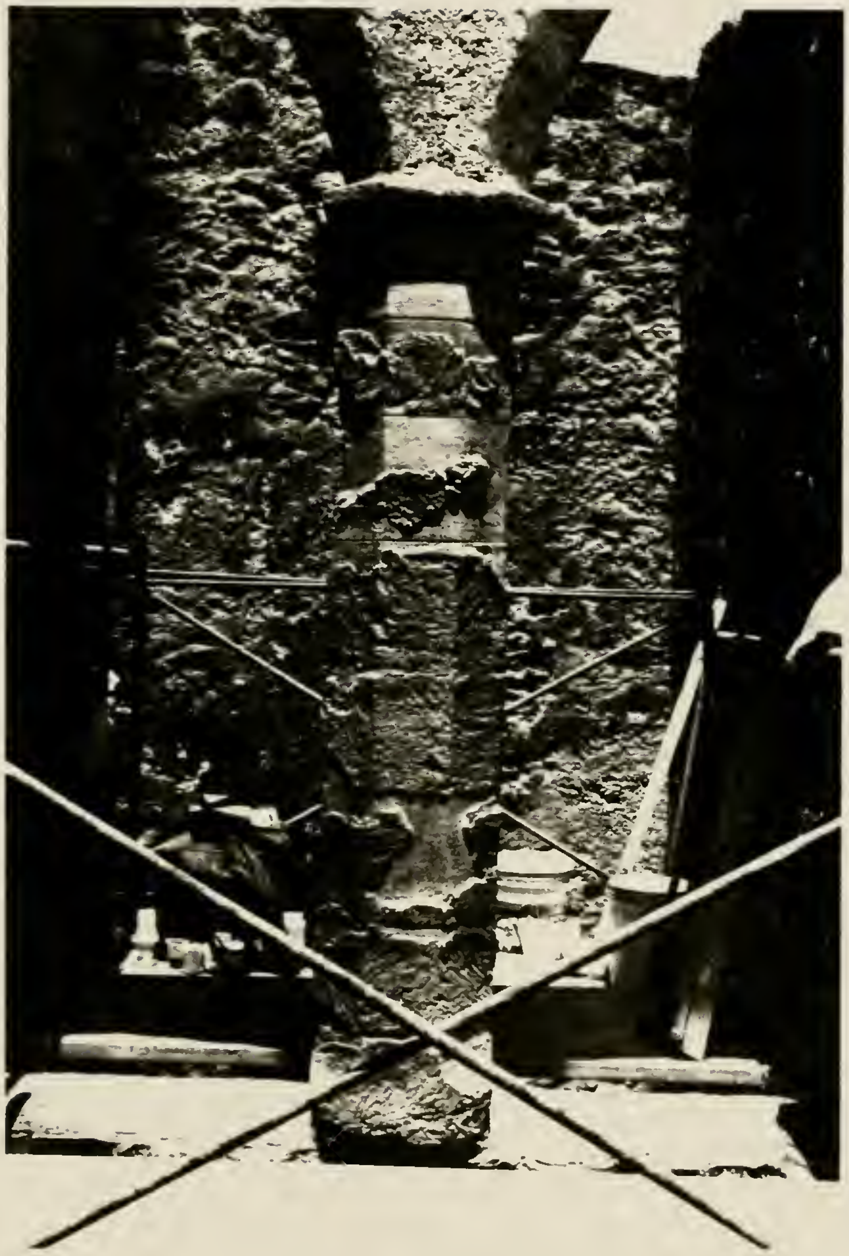

Figure 3.3 South elevation of the convento column after conservation, May 1993.

Appendix A List of comparative studies of acrylic/silane mixtures: reference, type of stone, products compared, and tests conducted

Reference - **Rossi-Manaresi, 1976**

Type of stone - two sandstones from Bologna

Products compared - MTMOS (Rhodorsil X 54-802)
methyl phenyl polysiloxane (Rhodorsil XR-893)
mixture of MMA/methyl alkoxysilane (Paraloid B72 and Dri-Film 104)
mixture of silicone/acrylic (Mased Product 460)
mixture of ethyl silicate/MTEOS (Wacker H)
mixture of ethyl silicate/MTEOS (Tegovakon)
mixture of epoxy/ethyl silicate (Ciba Geigy Araldite DY 022 and Dynasil A)
aliphatic epoxy (Ciba Geigy Araldite XB 2697)
epoxy (Ciba Geigy LM 6121)
polyurethane (Metalfix Oxanpierre P/529/PIE)

Tests conducted - depth of penetration
porosity
compressive strength
water absorption
saturation coefficient
resistance to salt crystallization
color change

Reference - **Cuttano et al., 1981**

Type of stone - tuff from Matera, Italy

Products compared - mixture of MMA/methyl alkoxysilane (B72/Dri-Film 104)
mixture of ethyl silicate/MTEOS (Wacker H)
mixture of acrylic/silane (Mased Product 460)
methyl phenyl polysiloxane (Rhodorsil XR-893)
silicone (Rhodorsil AC-30)
epoxy solution (Products XG 40 and XG 41)
aluminum stearate (Transkote)
aluminum-magnesium fluorosilicate (Barrafluato)

Tests conducted- bulk density (percent absorption of materials)
water absorption
capillarity
resistance to salt crystallization
depth of penetration

Reference - **Gnudi et al., 1981**

Type of stone - marble, Istrian stone, Verona stone

Products compared - acrylic polymer (unspecified)

mixture of acrylic/silicone(unspecified)
mixture of MMA and methyl alkoxysilane (Paraloid B72 and Dri-Film 104)

Tests conducted - microstructure
porosity
water absorption
UV stability
resistance to salt crystallization

Reference - Charola et al., 1982

Type of stone - impure Egyptian limestone (high clay content)

Products compared - 15% PMMA in methylene chloride
MTMOS (Dow Corning Z6070)
mixture of acrylic/silane (Raccanello E55050)

Tests conducted - microstructure

Reference - Charola et al., 1984

Type of stone - oolitic Indiana limestone, fossiliferous Vicenza limestone

Products compared - MTMOS (Dow Corning T4-0149)
prepolymerized methyl alkoxysilane (Dri-Film 104)
mixture of MMA/MTMOS (Acryloid B72/Dow Corning T4-0149)
mixture of MMA/methyl alkoxysilane (B72/Dri-Film 104)

Tests conducted - microstructure

Reference - Bradley, 1985

Type of stone - Caen stone and an oolitic limestone

Products compared- MTMOS (Dow Corning Z6070)
ethyl silicate (Wacker OH)
mixture of MTMOS/acrylic silane (Dow Corning Z6070 and Raccanello Acrylic Silane E 55050?)
mixture of ethyl silicate/MTEOS (Wacker H)
catalysed systems of the above
alkyl alkoxysilane (Brethane)

Tests conducted - curing time
polymer yield (percent retention of material)
depth of penetration
color change
porosity

resistance to acid attack (immersion)
mechanical strength (qualitative)
immobilization of salts

Reference - Tucci et al., 1985

Type of stone - Indiana limestone, Vicenza limestone

Products compared - mixture of MMA/methyl alkoxysilane (Acryloid B72 and Dri-Film 104)

Tests conducted - UV resistance
acid fog resistance
microstructure

Reference - Nishiura, 1987

Type of stone - porous tuff (broken into small particles)

Products compared - MTEOS oligomer (SS-101)
MMA (Paraloid B72)
epoxy (Araldite CY230)
epoxy/MTEOS mixture (CY230 and SS-101)
MMA and MTEOS mixture (B72 and SS-101)
all of the above with two silane coupling agents

Tests conducted - abrasion resistance
resistance to freeze-thaw cycling

Reference - Wheeler et al., 1991

Type of stone - Wallace (Nova Scotia) sandstone, Salem (Indiana) limestone

Products compared - 10% MMA in toluene (Acryloid B72)
MTMOS (Dow Corning Z6070)
bisphenol A epoxy (Epoxy Technologies EPO-TEK 301)
mixtures of 5,10, and 30% MMA in MTMOS (B72 and Z6070)

Tests conducted - viscosity
vapor pressure (manometry)
reaction mechanisms and kinetics (percent retention of materials measured through gravimetry, evaporative loss through gas chromatography)
microstructure (interactions of materials during cure through silicon nuclear magnetic resonance spectroscopy, SEM)
modulus of rupture

Appendix B Experimental program data

Table B.1 Measurements of the depth of penetration of treatments in facsimiles (in reticle graduations)*

	depth of penetration			
D5.OH	80	95	80	
D6.OH	95	90	105	
D7.OH	113	125	120	
D8.OH	80	95	90	
D9.SQ	120	115	115	
D10.SQ	95	80	75	90
D11.SQ	100	100	115	110
D12.SQ	-	-	-	-
D13.MX	130	110	115	
D14.MX	115	110	110	
D15.MX	100	135	130	
D16.MX	90	125	110	

* One reticle graduation equals 0.025 mm.

Table B.2 Measurements of decreases in water absorption and increases in bulk specific gravity of facsimiles

	absorption, weight %	bulk specific gravity
N5.OH	7.12	2.11
N6.OH	7.36	2.10
N7.OH	7.39	2.09
N8.OH	6.92	2.10
N9.SQ	0.40	2.12
N10.SQ	0.37	2.15
N11.SQ	0.39	2.15
N12.SQ	0.35	2.15
N13.MX	0.22	2.20
N14.MX	0.26	2.16
N15.MX	0.29	2.20
N16.MX	0.40	2.19

Table B.3 Corrected measurements of weight loss of facsimiles due to water vapor transmission (in grams)

Day	V2.CT	V3.CT	V4.CT	V6.OH	V7.OH	V8.OH
1	297.53	297.65	304.58	309.39	307.21	303.94
2	297.00	297.17	303.99	309.22	306.99	303.64
3	296.38	296.54	303.46	308.84	306.62	303.26
5	294.89	295.55	302.57	308.20	305.97	302.53
6	293.32	294.55	301.89	307.70	305.57	302.14
7	292.58	293.82	301.24	307.30	305.20	301.71
8	291.88	293.15	300.59	306.94	304.86	301.34
10	290.39	291.85	299.31	306.07	304.04	300.42
13	287.74	289.76	297.26	304.77	302.76	299.06
14	286.93	289.01	296.56	304.34	302.34	298.65
15	286.33	287.51	296.02	304.01	301.96	298.23
17	285.09	286.05	294.99	303.25	301.21	297.42
20	283.19	283.98	293.30	302.31	300.17	296.22
21	282.70	283.39	292.54	301.83	299.68	295.79
22	281.93	282.64	291.93	301.33	299.32	295.35
23	280.35	282.02	290.84	300.95	298.98	294.90

Day	V10.SQ	V11.SQ	V12.SQ	V14.MX	V15.MX	V16.MX
1	307.24	309.11	300.44	306.40	315.76	309.31
2	307.23	309.17	300.48	306.40	315.79	309.34
3	307.14	308.98	300.30	306.16	315.60	309.15
5	306.86	308.83	300.12	305.88	315.22	308.93
6	306.62	308.60	299.86	305.48	314.84	308.59
7	306.46	308.42	299.64	305.21	314.64	308.37
8	306.41	308.36	299.46	305.01	314.51	308.27
10	306.21	308.02	298.94	304.50	314.05	307.87
13	305.57	307.48	298.47	303.68	313.26	307.09
14	305.20	307.26	298.10	303.45	312.99	306.86
15	304.93	307.06	297.85	303.13	312.75	306.57
17	304.38	306.69	297.33	302.62	312.30	306.03
20	303.77	306.22	296.59	302.01	311.76	305.30
21	303.53	305.96	296.23	301.73	311.48	305.05
22	303.27	305.79	296.01	301.46	311.29	304.78
23	302.89	305.61	295.75	301.19	311.06	304.49

Table B.4 Measurements of weight loss of facsimiles due to salt crystallization (in grams)

Day	S5.OH	S6.OH	S7.OH	S8.OH	S9.SQ	S10.SQ
1	257.07	258.20	265.46	287.06	272.92	259.58
2	257.45	258.56	266.10	290.02	274.53	260.74
3	262.12	267.91	271.52	289.44	273.00	259.83
4	268.61	267.34	278.39	296.85	270.92	257.91
5	267.58	265.19	276.87	289.35	267.99	254.95
6	268.55	265.26	278.04	286.73	268.60	255.49
7	73.77	262.49	275.56	238.79	268.49	255.45
8	63.78	132.34	78.67		268.82	255.82
9					269.30	256.47
10					269.16	256.54
11					266.85	254.20
12					267.39	254.69
13					264.18	250.00
14					262.29	242.72
15					260.50	216.45
16					239.82	199.72
17					217.60	182.76
18					212.62	167.59

Day	S11.SQ	S12.SQ	S13.MX	S14.MX	S15.MX	S16.MX
1	266.67	266.52	265.98	287.79	294.48	268.60
2	268.89	267.52	266.23	287.91	294.91	268.84
3	267.38	266.42	265.49	287.32	293.95	268.18
4	265.19	264.81	264.90	286.71	293.16	267.82
5	261.78	262.44	263.70	285.36	291.80	266.91
6	262.22	262.85	263.74	285.50	291.70	266.94
7	262.12	262.60	263.63	285.37	291.37	266.73
8	262.56	262.88	263.83	285.69	291.74	267.04
9	263.13	263.30	264.14	286.10	292.04	267.90
10	263.50	263.29	266.59	288.34	293.15	270.61
11	260.29	260.79	262.50	283.79	289.07	263.95

Table B.4 (continued)

Day	S11.SQ	S12.SQ	S13.MX	S14.MX	S15.MX	S16.MX
12	258.96	261.39	263.39	284.60	289.37	261.42
13	255.83	259.04	258.42	278.75	283.49	254.91
14	250.48	258.03	255.29	278.01	281.18	251.35
15	234.25	254.60	243.36	275.07	253.10	245.95
16	216.68	251.00	206.85	266.76	240.62	239.51
17	146.28	249.00	107.50	141.43	208.58	233.84
18	137.41	246.27	100.78	125.38	201.50	228.82

Appendix C Survey of pretreatment conditions of the convento column, Mission San José y San Miguel de Aguayo, Texas

Appendix C Survey of pretreatment conditions

A survey of the condition of the column prior to treatment was conducted visually and recorded in a graphic format. The conditions which were located and defined in the survey provided answers to the nature and the causes of deterioration of the column. As well, the conditions mapped on the survey dictated both the nature and the location of specific conservation treatments.

Eight conditions were identified on the column; these are explained below:

> *original tooled surface*: faces of the drums retaining their original surface as characterized by tooling marks; these surfaces also preserve the original planes of the drum surfaces. Roughly 30% of all original surfaces were intact. The greatest amount of original surface was on the south, southeast, and southwest faces of the drums, the least on the north and northwest faces. The capital of the column retains nearly 100% of its original surface because no gypsum was used above it and thus solubilized salts did not enter the stone.
>
> *gypsum patch or bedding mortar*: used originally as a bedding mortar, thus found in narrow horizontal joints and in large vertical header joints between the halves of the second, fourth and sixth drums from the base. Also used in the first repairs to the column as evidenced by 1927 photographs; many of these patches have been lost, and those that remained were weathered.
>
> *lime patch*: soft but relatively sound material used in the second repair of the column; much gypsum lay beneath these patches. Although sound themselves,

the lime patches rang hollow, indicating detached surfaces below. When the patches were removed, the exposed surfaces of stone displayed extensive scaling and flaking.

cracking: this condition pertains only to large cracks, which were quite limited. An infinite number of microcracks existed but these resulted in *scaling and flaking*, and are identified under that heading.

detached area > 1/8 inch: occurring on all surfaces and essentially large microcracks into which adhesive solutions could be injected.

detached area < 1/8 inch: occurring mostly along the edges of original surfaces; separations large enough to accept grout mixture.

scaling and flaking: the result of microcracking and subsequent delamination of many thin layers after the loss of the somewhat harder and more resistant original surface, producing very friable surfaces deteriorated to a depth of 20 to 50 mm. Original surfaces never displayed this condition, but frequently overlaid the condition; all surfaces which had lost their original finish and had either not been patched or had lost their patches displayed this condition. Beneath most lime and gypsum patches, the condition was quite severe.

biological growth: black lichen present on most north-facing original surfaces and on almost all lime patches.

Graphic documentation of pretreatment conditions is contained in the final project report

prepared for San Antonio Missions National Historical Park, Southwest Region, National Park Service (Brackin, 1993).

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